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ABSTRACTS OF CHEMICAL PAPERS PUBLISHED IN BRITISH AND FOREIGN JOURNALS.

PART I.

Organic Chemistry.

The Addition of Hydrogen Bromide to Allyl Bromide. A. F. HOLLEMAN and B. F. H. J. MATTHES (*Proc. K. Akad. Wetensch. Amsterdam*, 1918, **21**, 90—91).—In bright light, hydrogen bromide is absorbed by allyl bromide with the almost quantitative formation of trimethylene bromide, b. p. 167·1°/760 mm.; in the dark, on the other hand, absorption proceeds much more slowly and, whilst trimethylene bromide is the main product, considerable amounts of propylene bromide are also formed. H. W.

Monohydrochloride of Isoprene. OSSIAN ASCHAN (*Ber.*, 1918, **51**, 1303—1307).—Isoprene, which had been prepared from commercial *d*-limonene by means of the isoprene lamp and kept for four years at 4—8°, was fractionated and the portion, b. p. 34—35·5°, D_4^{20} 0·6765, was mixed with 6% of dry ether, cooled in a mixture of snow and sodium chloride, and treated with hydrogen chloride. The product, after being washed with water and dried, was fractionated. The first three fractions, b. p. 65—90°, were treated again in the same way. The fraction, b. p. 107—110°, contains *isoprene monohydrochloride*, C_5H_9Cl, b. p. 109°, D_4^{20} 0·9335, which has an odour resembling that of allyl chloride, combines with hydrogen chloride to form isoprene dihydrochloride (Bouchardat's dichloro*iso*pentane), b. p. 145—146°, D_4^{20} 1·0654, and reacts with bromine in cold chloroform to form a yellow, viscous oil, $C_5H_9ClBr_2$, which cannot be distilled without decomposition.

The isoprene monohydrochloride, b. p. 85—91°, D 0·868, described by Bouchardat in 1879, was almost certainly *tert.-iso*amyl chloride. Isoprene prepared from *d*-limonene as above contains β-methyl-Δ^{β}-butylene. C. S.

Optically Active Propylene Glycol and Optically Active β-Hydroxybutyric Acid. EMIL ABDERHALDEN and EGON EICHWALD (*Ber.*, 1918, **51**, 1312—1322).—The specific rotations of the optically active fats previously prepared (A., 1914, i, 801) are unexpectedly small, and active propylene glycol has therefore been prepared in the hope that from it will be obtained more suitable substrates for the study of ferment action.

The desired glycol cannot be isolated from the mixture obtained by the action of nitrous acid on optically active propylenediamine.

Attempts to resolve β-bromo-*n*-propylamine by tartaric, bromocamphorsulphonic, or bromosuccinic acid, formyl-leucine, or similar compounds failed, uncrystallisable syrups being obtained; the resolution of β-chloro-*n*-propylamine, however, is readily effected. A solution of allylamine hydrochloride is saturated at 0° with hydrogen chloride and heated in a sealed tube at 110—120° for five to six hours, the resulting β-chloro-*n*-propylamine is isolated and treated in ether–alcohol solution with *d*-tartaric acid (1 mol.); the precipitate, after being recrystallised ten times from hot water, yields a d-*tartrate*, m. p. 109·5°, $[\alpha]_D^{18}$ +36·72° in water, from which d-*β-chloro*-n-*propylamine hydrochloride*, $C_3H_9NCl_2$, m. p. 179·5°, $[\alpha]_D^{18}$ +34·80° in water, is prepared. An aqueous solution of the *d*-tartrate at about 10° is converted by sodium nitrite into d-*β-chloro-α-propanol*, b. p. 40—41°/15 mm., $[\alpha]_D^{18}$ +9·26°. Since the latter could not be obtained quite pure it was added to aqueous potassium hydroxide at 50—70°, and thus converted into d-*propylene oxide*, b. p. 36·5—38°, $[\alpha]_D^{18}$+12·72°, which has been prepared by Le Bel in a very impure state by fermentation. *d*-Propylene oxide is extensively racemised by water, and on this account must be removed by distillation as rapidly as possible from the aqueous alkali employed in its preparation (above). When added slowly to well-cooled, anhydrous formic acid, it is converted into the formate of propylene glycol, which is readily hydrolysed by 15% hydrochloric acid, yielding d-*propylene glycol*, b. p. 95°/15 mm., $[\alpha]_D^{18}$ +13·71° in water. The *d*-glycol reacts with butyryl chloride in chloroform solution to form d-*propylene glycol dibutyrin*, $C_{11}H_{20}O_4$, b. p. 95—105°/15 mm., α +2·05° in 1-dcm. tube.

The following *l*-compounds are described: l-*β-chloro*-n-*propylamine hydrochloride*, $[\alpha]_D^{18}$ −17·07° in water; l-*β-chloro-α-propanol*, $[\alpha]_D^{18}$ −2·92°; l-*propylene oxide*, $[\alpha]_D^{18}$ −8·26°; l-*propylene glycol*, $[\alpha]_D^{18}$ −8·97° in water.

A synthesis of the optically active, biologically important β-hydroxybutyric acid has been effected and its configuration determined. The addition of hydrogen cyanide to *d*-propylene oxide does not lead to a satisfactory result. *d*-Propylene oxide was therefore converted by cold hydrobromic acid into l-*β-bromo*iso*propyl alcohol*,

$OH\cdot CHMe\cdot CH_2Br$, b. p. 45—50°/15 mm., α $-2{\cdot}05°$ in 1-dcm. tube, which reacts readily with potassium cyanide in boiling alcohol to give l-β-*hydroxybutyronitrile*, b. p. 99—100°/15 mm., $[\alpha]_D^{18}$ $-10{\cdot}03°$ in water. The last substance is hydrolysed by hot concentrated hydrochloric acid, and yields *l*-β-hydroxybutyric acid, the sodium salt of which has $[\alpha]_D^{18}$ $-13{\cdot}28°$ in water.

d-β-Chloro-α-propanol is oxidised by ammonium dichromate and dilute sulphuric acid at the ordinary temperature, and yields *l*-α-chloropropionic acid, which is converted into *l*-alanine by aqueous ammonia.

The preceding configurative relations are shown thus:

d-propylene oxide → *l*-β hydroxybutyric acid
l-β-Chloro-α-propanol
l-α-chloropropionic acid → *l*-alanine

C. S.

Synthesis of Optically Active Glycerophosphoric Acid. EMIL ABDERHALDEN and EGON EICHWALD (*Ber.*, 1918, **51**, 1308—1312).—Since the naturally occurring glycerophosphoric acid is optically active (Willstätter and Lüdecke, A., 1904, i, 1067), one of the first steps in the synthesis of a phosphatide must be the synthesis of glycerophosphoric acid in the optically active form. The authors, employing the optically active halogenhydrins and epihydrins previously prepared by them (A., 1914, i, 801), obtained unsatisfactory results when they attempted to add phosphoric acid to *l*-epihydrin alcohol, epichlorohydrin, or epibromohydrin, and unsuccessful results when they attempted to esterify monochlorohydrin or monobromohydrin with anhydrous phosphoric acid, but achieved success by using Fischer's pyridine–phosphoryl chloride method. Phosphoryl chloride is added slowly to a solution of *d*-α-bromohydrin in dry pyridine, the temperature being kept below $-10°$; ice-water is added after one to two hours, the solution is shaken with sufficient silver to remove the chlorine (an excess must be avoided), filtered, treated with hydrogen sulphide, again filtered, and evaporated in a vacuum to remove the hydrogen sulphide and a portion of the pyridine. Barium hydroxide in excess is added, the mixture is diluted, and then concentrated in a vacuum to remove the remainder of the pyridine; the barium in the filtered solution is exactly precipitated with sulphuric acid, and after filtering again the filtrate is without delay treated with 10% lithium hydroxide solution, after twenty-four hours evaporated to a small volume in a vacuum, heated at 80° for one hour, cooled, neutralised with hydrobromic acid, and evaporated in a vacuum until crystals begin to appear; these are redissolved by adding a few c.c. of water, and the filtered solution is treated with alcohol. The precipitate is dissolved in water and precipitated by alcohol, and after a repetition of this treatment is free from lithium bromide. The product is

nearly pure *lithium* d-*glycerophosphate*, $C_6H_7O_6PLi_2$, $[\alpha]_D^{18}$ $+3{\cdot}51°$ in aqueous solution. *Lithium* l-*glycerophosphate* was also prepared, having $[\alpha]_D^{18}$ $-3{\cdot}02°$. By using alcoholic instead of aqueous lithium hydroxide, a glycerophosphate having $[\alpha]_D^{18}$ $+6{\cdot}26°$ was obtained, but the higher value may be due to a partial conversion of the glycerophosphate into the epihydrinphosphate,

$$\left.\begin{matrix}CH_2\\ \mid \\ O\end{matrix}\right>CH{\cdot}CH_2{\cdot}O{\cdot}PO(OLi)_2.$$

C. S.

Preparation of Ethyl Acetate from Acetaldehyde. FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P., 308043; from *Chem. Zentr.*, 1918, ii, 693).—The process depends on the use of a solution of aluminium ethoxide, $Al(OEt)_3$, which contains at the most only traces of halogen compounds, in an organic solvent of high boiling point, such as solvent naphtha. With such solutions, which allow the most favourable temperature to be readily maintained, the yield of practically pure ethyl acetate exceeds 85% of that theoretically possible; at the same time, the duration of the action is considerably decreased, and the consumption of aluminium ethoxide is reduced to 3—5% of the acetaldehyde. H. W.

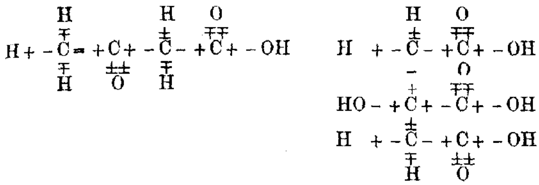
The Velocity of Hydration of the Anhydrides of some Fatty Acids. P. E. VERKADE (*Rec. trav. chim.*, 1918, **37**, 315—354).—A theoretical discussion of work already published (compare A., 1914, ii, 256; 1916, ii, 234, 607), in which the author shows that the process of hydration is much more complicated than is shown by the equation $(R{\cdot}CO)_2O + H_2O = 2R{\cdot}CO_2H$. W. G.

Configuration of Organic Compounds and their Relation to Chemical and Physical Properties. II. ARTHUR MICHAEL (*J. Amer. Chem. Soc.*, 1918, **40**, 1674—1707).—A continuation of the theoretical discussion of the subject (compare A., 1918, i, 249). The relationship between the configuration of unsaturated acids and their physical properties (density, m. p., b. p., viscosity, optical activity, magnetic rotation) is examined, and the connexion between configuration and chemical properties (addition, stereomutation, catalysis, esterification) discussed. H. W.

Determination of the Configuration of *cis-trans*-Isomeric Substances. J. BÖESEKEN and CHR. VAN LOON (*Proc. K. Akad. Wetensch. Amsterdam*, 1918, **21**, 80—89).—A theoretical paper, in which the methods of determining the configuration of *cis-trans* isomerides are critically discussed and their applicability to various types of compounds considered. H. W.

Electronic Constitutions of Acetoacetic and Citric Acids and some of their Derivatives. MILTON TH. HANKE and KARL K. KOESSLER (*J. Amer. Chem. Soc.*, 1918, **40**, 1726—1732).—A consideration of the formation of acetonedicarboxylic acid from citric

acid, of its relationships to acetone and acetoacetic acid, of the connexion between the latter and acetic acid, and of those between acetic acid and keten, leads the author to propose the electronic formulæ (I) and (II) for acetoacetic and citric acids respectively:



(I.) (II.)

H. W.

Pasteur's Principle of the Relation between Molecular and Physical Asymmetry. V. Optically Active Complex Salts of Iridium-trioxalic Acid. F. M. JAEGER (*Proc. K. Akad. Wetensch. Amsterdam*, 1918, **21**, 203—214).—Racemic potassium iridium oxalate, $K_3[Ir(C_2O_4)_3],4\frac{1}{2}H_2O$ (A., 1918, i, 4), has been resolved into its optically active components by means of the strychnine salt, thus demonstrating for the first time the possibility of a partial asymmetry in the case of iridium as the central atom.

Strychnine d-*iridium oxalate*, $(C_{21}H_{22}O_2N_2)_3[Ir(C_2O_4)_3],3\frac{1}{2}H_2O$, forms pale yellow, very fine needles; the corresponding l-*salt* $(+3H_2O)$ crystallises in somewhat thicker needles.

d-*Potassium iridium oxalate* $(+H_2O)$, large orange-coloured, flattened, triangular bipyramids $(a:c=1:0{\cdot}9520;\ \alpha=100°20')$, has D^{20} 2·734; the corresponding *l*-salt is also described. As in the case of the oppositely rotating rhodium salts (A., 1918, i, 3), a non-superposable hemihedrism accompanies the contrary power of rotation.

The specific rotation of the salts in aqueous solution for differing concentrations and for light of varying wave-length has been investigated, and the results are given in a series of tables and graphs, for details of which the original communication must be consulted. In the case of the potassium salts, the slope of the graph is quite different from that found with the corresponding rhodium salt, thus showing the preponderating influence of the special nature of the central metallic atom on the specific light absorption (colour) of these salts and on the whole character of the rotation dispersion.

H. W.

Pasteur's Principle of the Relation between Molecular and Physical Asymmetry. VI. The Fission of Potassium Rhodium Malonate into its Optically Active Compounds. F. M. JAEGER and WILLIAM THOMAS (*Proc. K. Akad. Wetensch. Amsterdam*, 1918, **21**, 215—224).—The resolution of *r*-potassium rhodium malonate, $[Rh(C_3H_2O_4)_3]K_3,3H_2O$ (A., 1918, i, 4), is effected

through the cinchonine salts and subsequent decomposition of the latter by potassium iodide. *Cinchonine* l-*rhodium malonate* ($+\frac{1}{2}H_2O$) is less soluble in water and less stable to heat than the corresponding *d*-salt ($+3H_2O$). d- and l-*Potassium rhodium malonates* form pale yellow crystals; measurements of the *l*-salt showed the crystals to belong to the monoclinic–sphenoidal class ($a:b:c = 1{\cdot}0637:1:1{\cdot}1667$, $\beta = 82°27\frac{1}{4}'$), D_4^{18} 2·317.

The molecular rotation dispersion of the salts has been investigated in aqueous solution; with the potassium salts a remarkable maximum occurs at about 5800 Å.U. For wave-lengths smaller than 5800 A.U. the rotation of the plane of polarisation increases with increasing wave-length, whilst for those greater than 5800 A.U. it diminishes with increasing wave-lengths as in ordinary cases. In the neighbourhood of 5800 A.U. the absorption-spectrum, however, does not manifest a single line or band. The occurrence of such anomalous rotation-dispersion seems to be theoretically explicable if the assumption may be made that at least two kinds of active ions are present. H. W.

New Synthetic Passage from Aliphatic to Aromatic Compounds. TEL. KOMNINOS (*Compt. rend.*, 1918, **167**, 781—783; *Bull. Soc. chim.*, 1918, [iv], **22**, 449—455).—Malonyl chloride and acetone react together in the presence of calcium carbonate to give phloroglucinol and a *compound*, $CH_3{\cdot}CO{\cdot}CH_2{\cdot}CO{\cdot}CH_2{\cdot}COCl$, which when boiled with water and some more calcium carbonate, in its turn is converted into phloroglucinol. W. G.

Effect of Sodium on Mixtures of Malonic and Succinic Esters. GERALD E. K. BRANCH and H. E. HUDSON BRANCH (*J. Amer. Chem. Soc.*, 1918, **40**, 1708—1713).—The investigation was undertaken in the hope of the ultimate synthesis of the compound, $\begin{matrix}CH{=}CH\\ | \qquad\quad \\ CH{=}CH\end{matrix}\!\!>CH{-}CH<\!\!\begin{matrix}CH{=}CH\\ \qquad\quad | \\ CH{=}CH\end{matrix}$, which might show a tendency to break down to give the *cyclo*pentadienyl radicle. The condensation of ethyl malonate with ethyl succinate was studied as the first step in this direction. The results were not very promising, and the observations may be summarised as follows: (1) When molar mixtures of malonic and succinic esters are treated with sodium, the main product is succinylsuccinic ester. (2) When a large excess of malonic ester is used, phloroglucinoltricarboxylic ester is produced. (3) *Malonylsuccinic ester*, yellow crystals, m. p. 163°, is obtained from succinylsuccinic and malonic esters. The results are to be explained by an application of Dieckmann's theory of the reversibility of the acetoacetic ester condensation. H. W.

Preparation of Derivatives of Cystine, Soluble in Water. BERNHARD STUBER (D.R.-P. 307858; from *Chem. Zentr.*, 1918, ii, 574).—The sparingly soluble compounds of cystine and its derivatives with mercury, mercury chloride, or silver are dissolved in solutions of sodium chloride, sodium bromide, sodium thio-

cyanate, or lithium chloride, and the solutions are treated with an excess of acetone, methyl or ethyl alcohol, or ether; the precipitates are filtered and dried in a vacuum. Complex salts of amphoteric character are obtained which are expected to find therapeutic application. The following substances are particularly described: *cystinemercury sodium chloride*, yellow powder; *cystinemercury sodium bromide*, brown powder; *cystinemercury lithium chloride*, yellowish-white powder; *cystinemercury sodium thiocyanate*, yellowish-brown powder; *cystinesilver sodium chloride*, brown powder; *cystinemercury chloride sodium chloride*, white powder; *cystinemercury chloride sodium bromide*, brown powder. H. W.

Reducibility of Formic Acid. K. A. HOFMANN and HELGE SCHIBSTED (*Ber.*, 1918, **51**, 1389—1398).—In spite of all statements in the literature to the contrary, the authors have never obtained more than 4% of the expected yield in their attempts to reduce formic acid to formaldehyde and methyl alcohol by hydrogen under the most diverse experimental conditions. The following reducing agents were tried: (i) reduction of formic acid in aqueous solution by nascent hydrogen at ordinary pressure; the hydrogen was generated by zinc in contact with mercury, cadmium, copper, and vanadium oxide, with and without the addition of dilute sulphuric acid, by zinc and palladous chloride, by zinc dust with and without the addition of palladium, and by the platinum metals; (ii) reduction of formic acid in aqueous solution by nascent hydrogen under increased pressure; the experiments under (1) were repeated in sealed tubes at 70°, the tubes being filled with carbon dioxide before sealing; (iii) reduction with simultaneous catalytic fission of the formic acid; the experiments under (ii) were repeated in the presence of platinum metals on porous tile. C. S.

Production of Formaldehyde and Methyl Alcohol from Formates. K. A. HOFMANN and HELGE SCHIBSTED (*Ber.*, 1918, **51**, 1398—1418. Compare preceding abstract).—In the well-known decomposition of formic acid by heat and the reaction between an alkali formate and an alkali hydroxide, the principal factor controlling the course of the reactions is the striving to produce the stable hydrogen molecule. Metallic formates, however, are able, to a degree dependent on the nature of the particular metal, to yield formaldehyde according to the equation

$$2H{\cdot}CO_2M = M_2CO_3 + CH_2O;$$

the secondary decomposition, $CH_2O = H_2 + CO$, can be reduced to a minimum under suitable experimental conditions, and the decomposition in the presence of water, $CH_2O + H_2O = CO_2 + 2H_2$, can be prevented altogether.

The temperature at which a distinct and sustained evolution of gas begins from the formates is in general higher the more strongly basic is the metallic oxide; thus copper formate (170°) is the first and potassium formate (375°) the last member of the series of formates examined. The formaldehyde produced experiences, according to the nature of the metalliferous residue, diverse trans-

formations, of which the most important is its conversion into methyl alcohol and formic acid. In the case of the formates of strong bases, only a little formaldehyde is obtained, the main products being methyl alcohol, acetone, furfuraldehyde, empyreumatic substances, and carbon.

Zinc formate is the most suitable substance for the production of formaldehyde and methyl alcohol, and its decomposition is described in detail. Methyl formate has been detected in the products.

The vapour of formic acid in the presence or absence of hydrogen is converted by chemically unchangeable catalysts, such as asbestos, platinised asbestos, alumina, carbon, etc., almost exclusively into carbon monoxide and steam or carbon dioxide and hydrogen as soon as the temperature is high enough to bring the formic acid into reaction. If, however, the catalyst and the temperature of reaction are so selected that the formation of formates is rendered possible, the production of considerable quantities of formaldehyde and methyl alcohol is observed. The best catalysts for this purpose are zinc oxide and thoria. A diagram is given in which are plotted the two curves connecting the percentage of formaldehyde and the percentage of total decomposition products with the decomposition temperatures, zinc oxide being the catalyst. The two curves produced backwards meet at a point corresponding with about a 12% yield of formaldehyde and a decomposition temperature of about 245°, showing that at this temperature formaldehyde is the only primary decomposition product of formic acid. [See also *J. Soc. Chem. Ind.*, 1918, 782A.]

C. S.

The Preparation of Ethylamine and of Diethylamine. EMIL ALPHONSE WERNER (T., 1918, **113**, 899—902).

Pasteur's Principle of the Relation between Molecular and Physical Asymmetry. VII. Optically Active Salts of the Triethylenediaminechromi-series. F. M. JAEGER and WILLIAM THOMAS (*Proc. K. Acad. Wetensch. Amsterdam*, 1918, **21**, 225—230).—The molecular rotation dispersion of the optically active triethylenediaminechromi-iodides in aqueous solution at different concentrations has been investigated, and the results are given in a series of graphs and tables; the substances were obtained by Werner's method (A., 1912, i, 417). It was not found possible to obtain measurable crystals of the active salts, partly owing to their great solubility and partly because of the readiness with which they decompose in aqueous solution, particularly under the influence of light. *r*-Triethylenediaminechromi-iodide,

$$[Cr\ en_3]I_3,H_2O,$$

forms orange to red rhombic-bipyramidal crystals ($a:b:c=0{\cdot}8632:1:0{\cdot}8652$); the crystals are pseudo-tetragonal and per-

ectly isomorphous with the corresponding crystals of the cobalti- A., 1915, i, 867) and of the rhodium (A., 1918, i, 7) compound.

H. W.

Biochemical Properties of Aminoglucose. A. CLEMENTI Arch. farm. sper. Sci. off., 1918, **25**, 225—230; from *Chem. Zentr.*, 1918, ii, 617).—Glucosamine hydrochloride behaves as a monobasic acid in the formol titration; Molisch's reaction is positive with the free base, but negative with the salts. Fermentation with brewer's yeast, without addition of toluene, is observed after more than seventy-two hours; obviously, foreign micro-organisms are active, possibly owing to deaminisation. H. W.

Fluorides of Organo-metallic Compounds. I. Tin Trialkyl Fluorides and Tin Dialkyl Difluorides. ERICH KRAUSE *Ber.*, 1918, **51**, 1447—1456).—The fluorides exhibit striking differences in properties from the other tin alkyl and aryl haloids. Thus the tin trialkyl fluorides are solid, crystalline, odourless substances of high m. p., which sublime before fusing, are appreciably soluble in water, giving acid solutions, and are sparingly so in indifferent organic solvents such as benzene and ether, but dissolve more readily in the alcohols and glacial acetic acid. The tin dialkyl difluorides exhibit similar properties, and, in addition, form double compounds with alkali fluorides.

The tin trialkyl fluorides are precipitated quantitatively by treating solutions of the corresponding hydroxides (Grüttner and Krause, A., 1918, i, 158) with aqueous hydrofluoric acid, but can be obtained much more conveniently by treating alcoholic solutions of the other tin trialkyl haloids with an excess of a neutral aqueous solution of potassium fluoride. The latter reaction is reversible, and a complete reconversion of the fluoride into another tin trialkyl haloid is effected by warming with the concentrated halogen acid.

Tin dialkyl difluorides are precipitated almost quantitatively by treating alcoholic solutions of the other dihaloids with the calculated quantity of potassium fluoride in neutral aqueous solution.

The following compounds are described. All m. p.'s were determined in closed capillary tubes. *Tin trimethyl fluoride*, $SnMe_3F$, colourless prisms, which begin to darken at 360° and blacken at about 375°; *tin triethyl fluoride*, prisms, m. p. 302° (corr.); *tin tri-n-propyl fluoride*, prisms or needles, m. p. 275° (corr.); *tin triisobutyl fluoride*, prisms, m. p. 244° (corr.); *tin triisoamyl fluoride*, needles, m. p. 288° (corr.); *tin diethyl n-propyl fluoride*, long needles, m. p. 271° (corr.); *tin dimethyl difluoride*, colourless leaflets, decomp. above 360°; *tin diethyl difluoride*, tufts of needles or rhombic plates, m. p. 287—290° (uncorr.), sintering at about 240° (the double *salt*, $SnEt_2F_2,2KF$, forms stout leaflets); *tin di-n-propyl difluoride*, leaflets, m. p. 204—205° (uncorr.), sintering at 200°.

The tin trialkyl fluorides, which are easily obtained pure, are

available for the preparation of mixed tin tetra-alkyls, tin triethyl *n*-propyl, for example, being obtained from magnesium *n*-propyl chloride and tin triethyl fluoride in the usual way; the odour of the volatile tin trialkyl chloride is always observed, indicating that a partial exchange of the halogen atoms occurs.

*Tin tetra*iso*amyl*, prepared from tin tetrachloride and magnesium *iso*amyl chloride, and freed from any tin trialkyl haloid by aqueous-alcoholic potassium fluoride, has b. p. 188°/24 mm., $D_4^{19\cdot6}$ 1·0353, n_α 1·46946, n_D 1·47242, n_β 1·47989, n_γ 1·48607 at 16·0°. C. S.

Formation of Aromatic Hydrocarbons from Natural Gas Condensates. J. G. DAVIDSON (*J. Ind. Eng. Chem.*, 1918, **10**, 901—910).—Natural gas containing chiefly ethane and propane with small quantities of butane and pentane has been subjected to the "cracking" process at various temperatures in the presence of metals. The products of the reaction are gaseous and liquid, the latter being of a tarry nature and containing aromatic hydrocarbons. Both sets of products were analysed, and the results are tabulated in the paper. The experiments show that most metals are without action on the reaction. Paraffins ⟶ aromatic hydrocarbons. The metals nickel, iron, and cobalt are negative catalysts for the above reaction, but accelerate markedly the reaction paraffins ⟶ carbon + hydrogen. The effect of pressure and temperature on the reaction has been studied, and it is shown that the temperature 850° is the most favourable for the production of liquid tar, and that the formation of complex aromatic substances increases with the temperature. Increase of pressure inhibits the formation of tar, whilst diminished pressure increases the yield of unsaturated substances, but also decreases the actual yield of tar. Butadiene has been isolated in fairly large amounts from the unsaturated compounds produced in the thermal decomposition of the natural gas condensate. Acetylene is without action in the formation of aromatic hydrocarbons. Tar containing aromatic substances has been produced from the "cracking" of a mixture of butadiene and ethylene. The most probable reaction for the formation of aromatic substances from natural gas condensate is:

$$\underset{\text{(Ethane.)}}{\left\{\begin{array}{c}\text{Saturated straight chain}\\ \text{hydrocarbons}\end{array}\right\}} \longrightarrow \underset{\text{(Ethylene.)}}{\left\{\begin{array}{c}\text{Simple}\\ \text{olefines}\end{array}\right\}} \longrightarrow$$

$$\underset{\text{(Butadiene.)}}{\left\{\begin{array}{c}\text{Higher olefines with}\\ \text{conjugated bonds}\end{array}\right\}} \longrightarrow \underset{\text{(Benzene.)}}{\left\{\begin{array}{c}\text{Aromatic}\\ \text{hydrocarbons}\end{array}\right\}}$$

J. F. S.

Dinitro-derivatives of *p*-Dichlorobenzene. 1 : 4-Dichloro-2 : 5-dinitrobenzene. EDITH H. NASON (*J. Amer. Chem. Soc.*, 1918, **40**, 1602—1605).—Of the possible 1 : 4-dichlorodinitrobenzenes, 1 : 4-dichloro-2 : 6-dinitrobenzene, m. p. 104°, has been

previously described and fully orientated; a second isomeride, m. p. 101°, has also been obtained, but its constitution has not been elucidated. The author now shows that all three isomerides are formed when *p*-dichlorobenzene is nitrated with a mixture of concentrated sulphuric and fuming nitric acids, and that the chief product is the previously unknown 1:4-*dichloro*-2:5-*dinitrobenzene*, fine, yellow needles, m. p. 81°. The constitution of the compound is deduced from its reduction to 2:5-dichloro-*p*-phenylenediamine (compare Mohlau, A., 1886, 941), and confirmed by oxidation of the latter substance to *p*-dichlorobenzoquinone, yellow crystals, m. p. 161°.

The isomeride, m. p. 101°, must therefore be 1:4-dichloro-2:3-dinitrobenzene. H. W.

s-Chlorobenzenedisulphonic Acid and some of its Derivatives. S. C. J. OLIVIER (*Rec. trav. chim.*, 1918, **37**, 307—314).—When chlorobenzene is heated with five times its volume of fuming sulphuric acid, containing 20% of sulphur trioxide, at 300° for six hours, the product is 5-*chlorobenzene*-1:3-*disulphonic acid*, decomposing at 100°, isolated as its *barium* salt, $C_6H_3Cl(SO_3)_2Ba,3H_2O$. It gives a *potassium* and an *ammonium* salt, a *dichloride*, m. p. 105·5—106°, and a *diamide*, m. p. 223—224°. The dichloride, when heated in a sealed tube with phosphorus pentachloride for four hours at 200—210°, yields *s*-trichlorobenzene.

4-Aminobenzene-1:3-disulphonic acid, when diazotised in hydrochloric acid solution and the diazonium salt decomposed with finely divided copper, gives 4-*chlorobenzene*-1:3-*disulphonic acid* isolated as its *potassium* salt. It gives a *dichloride*, an amorphous compound, and a *diamide*, m. p. 217—219°. W. G.

Studies in the Tetrahydronaphthalene Series. ARTHUR G. GREEN and FREDERICK MAURICE ROWE (T., 1918, **113**, 955—973).

Mono- and Di-chlorophenanthrenes. HÅKAN SANDQVIST and A. HAGELIN (*Ber.*, 1918, **51**, 1515—1526).—A solution of phenanthrene (containing anthracene; m. p. 97—102°) in carbon disulphide or carbon tetrachloride at 0° is treated slowly with an unsaturated solution of chlorine (about 1½ mols.) in the same solvent at 0°. In addition to unchanged phenanthrene the substances obtained are (1) a compound (? trichloroanthracene), pale yellow needles, m. p. 365° (corr.), (2) 9:10-dichloroanthracene (previously described by Sandqvist in 1917 as a dichlorophenanthrene, m. p. 208—209°), (3) phenanthrene 9:10-dichloride, (4) 10-chlorophenanthrene, (5) pitch.

Phenanthrene 9:10-dichloride, $C_{14}H_{10}Cl_2$, decomposes appreciably into 10-chlorophenanthrene and hydrogen chloride at the ordinary temperature in the course of a few days, the decomposition being catalytically accelerated by 10-chlorophenanthrene. The m. p. is

therefore variable; a carefully purified specimen had m. p. 161° (corr.; bath at above 150° and rapidly heated), and hydrogen chloride was liberated.

Pure 10-chlorophenanthrene can be prepared from the preceding dichloride at 150—175°. It forms long, colourless needles, m. p. 53—53·5° (corr.), b. p. 370° (corr.)/737 mm., D_4^{55} 1·2310 and D_4^{75} 1·2163. It yields phenanthraquinone by oxidation, and forms a *picrate*, $C_{14}H_9Cl,C_6H_2(NO_2)_3{\cdot}OH$, yellow, prismatic needles, m. p. 115° (corr.).

9:10-Dichlorophenanthrene, m. p. 160—160·5°, which is formed by chlorinating 10-chlorophenanthrene in cold carbon disulphide or tetrachloride, yields phenanthraquinone by oxidation with boiling acetic and chromic acids.

The 3:?-dichlorophenanthrene, m. p. 124°, obtained by Sandqvist (A., 1909, i, 779) is now proved to be I-3(or 6):10-dichlorophenanthrene, m. p. 125—125·5° (corr.), by its formation by heating I-10-chlorophenanthrene-3(or 6)-sulphonyl chloride with phosphorus pentachloride; it yields 3-*chlorophenanthraquinone*, orange-yellow needles, m. p. 261° (corr.) (*monoxime*, $C_{14}H_8O_2NCl$, yellow needles, m. p. 204° [decomp.]), by oxidation with chromic and acetic acids.

An aqueous solution of potassium phenanthrene-3-sulphonate on treatment at 50° with a cold saturated aqueous solution of chlorine yields *potassium* II-10-*chlorophenanthrene*-3(or 6)-*sulphonate*, small needles, which is converted by phosphorus pentachloride into II-10-*chlorophenanthrene*-3(or 6)-*sulphonyl chloride*, grey, crystalline powder, m. p. 171°, from which II-10-*chlorophenanthrene*-3(or 6)-*sulphonic acid*, m. p. 207°, is obtained by the action of water at 140—150°, and II-3(or 6):10-*dichlorophenanthrene*, colourless needles, m. p. 113°, by the action of phosphorus pentachloride. The last-mentioned compound yields 3-chlorophenanthraquinone by oxidation. (The prefixes I and II indicate: I, that the compound contains substituents having the same orientation as those in the 10-bromophenanthrene-3(or 6)-sulphonic acid obtained by the sulphonation of 10-bromophenanthrene; II, that the orientation of the substituents in the compound is the same as in the 10-bromophenanthrene-3(or 6)-sulphonic acid obtained by the bromination of phenanthrene-3-sulphonic acid). C. S.

Acetylation of *p*-Iodoaniline by Acetic Anhydride. P. J. MONTAGNE (*Ber.*, 1918, **51**, 1489—1492).—*p*-Iodoaniline, which is very conveniently prepared by treating a solution of *p*-iodonitrobenzene in acetone with a solution of stannous chloride in hydrochloric acid (D 1·19) and basifying after the acetone has spontaneously boiled, is converted by acetic anhydride into *p*-iodoacetanilide if the mixture is gently warmed, but into *p*-iodoacetanilide and *p*-iododiacetanilide if the mixture is boiled for one-quarter to six hours; a small quantity of a *substance*, leaflets, m. p. 204·5°, is also obtained.

p-Iodoacetanilide has m. p. about 170° (rapidly heated) and 184·5° (slowly heated). C. S.

Analgesic Substance and Process of Making. LAMBERT THORP (U.S. Pat., 1279942).—Anilides of α-bromo-α-ethylbutyric acid are prepared by treating arylamines with an acylhaloid of the acid. These anilides possess analgesic and sedative properties; they are decomposed on boiling with alkali hydroxide, the bromine being eliminated as alkali bromide. In particular, the *p*-phenetidide of α-bromo-α-ethylbutyric acid is specified; this is a colourless, crystalline compound slightly soluble in water, readily so in alcohol or ether, m. p. 54°. It has a peculiar, somewhat bitter taste. (See also *J. Soc. Chem. Ind.*, 1918.) J. F. B.

Trimorphic Change of 4-Nitroaceto-*o*-toluidide. FREDERICK DANIEL CHATTAWAY (T., 1918, **113**, 897—899).

The *n*-Butylarylamines. I. The Action of *n*-Butyl Chloride on *o*- and *p*-Toluidines. JOSEPH REILLY and WILFRED JOHN HICKINBOTTOM (T., 1918, **113**, 974—985).

The *n*-Butylarylamines. II. Nitration of Mono- and Di-*n*-butyl-*p*-toluidines. JOSEPH REILLY and WILFRED JOHN HICKINBOTTOM (T., 1918, **113**, 985—995).

Nitro-derivatives of Diphenylamine. HUGH RYAN and THOMAS GLOVER (*Proc. Roy. Irish Acad.*, 1918, **34**, [*B*], 97—105).—Considerable discrepancies are frequently noticed in the literature of the nitrodiphenylamines. With the object of removing these, the authors have prepared a series of substances by synthetic methods, that due to Goldberg (A., 1907, i, 1027) (in which aromatic amines are coupled with the halogen derivatives of aromatic nitro-compounds in nitrobenzene solution in the presence of potassium carbonate and cuprous iodide) being chiefly used. The following compounds are described: *p*-Nitrodiphenylamine, m. p. 133—134°, which, contrary to Goldberg's statement, yields a colourless solution in concentrated sulphuric acid; m-*nitrodiphenylnitrosoamine*, colourless, acicular crystals, m. p. 89—90°; 2:4-*dinitrodiphenylnitrosoamine*, pale yellow prisms, m. p. 149—151° (by the action of *iso*amyl nitrite on a cold solution of 2:4-dinitrodiphenylamine in glacial acetic acid; at a slightly higher temperature, 2:4:2′:4′-tetranitrodiphenylamine slowly separates); 3:4′-*dinitrodiphenylamine*, pale yellow crystals, m. p. 210—212°, after softening at 205°; 2:4:6-trinitrodiphenylamine, scarlet-red prisms, m. p. 178°; 2:4:3′-trinitrodiphenylamine, brown, platy crystals, m. p. 193—194°; *nitrophenyl*-2:4-*dinitro*-m-*tolylamine*, dark yellow prisms, m. p. 199° (slight decomp.); 4-*nitrophenyl*-2:4-*dinitro*-m-*tolylamine*, straw-coloured, prismatic needles, m. p. 210° (slight decomp.); 3-*nitrophenyl*-2:6-*dinitro*-m-*tolylamine* (?), prismatic needles, m. p. 199° (decomp.); 2:4:2′:4′-tetranitrodiphenylamine, brown prisms, m. p. 199—200°; 2:4:6:3′-tetranitrodiphenylamine, short, yellow prisms, m. p. 210° (corr.); 2:4:6:4′-tetranitrodiphenylamine, golden-yellow prisms, m. p. 222°.

m-Nitrodiphenylnitrosoamine is converted by nitric acid in glacial acetic acid solution into *trinitrodiphenylnitrosoamine*, yellow, pris-

matic needles, m. p. 184—185° (decomp.), after softening at about 179°.

2:4:3′-Trinitrodiphenylamine yields *tetranitrodiphenylamine*, yellow crystals, m. p. 190°, when treated with *iso*amyl nitrite. In similar circumstances, picryl-aniline gives two compounds, one of which, m. p. 236°, is probably 2:4:6:2′:4′:6′-*hexanitrodiphenylamine*, whilst the other, m. p. 193—194°, appears to be 2:4:6:2′:4′-pentanitrodiphenylamine. H. W.

The Freezing Points of Mixtures of Phenol, *o*-Cresol, *m*-Cresol, and *p*-Cresol. HARRY MEDFORTH DAWSON and CHRISTOPHER ARCHIBALD MOUNTFORD (T., 1918, **113**, 923—935).

Preparation of Hydroxy-alkyl Ethers of *p*-Acetylaminophenol or Substitution Products thereof. JOSEPH TCHERNIAC (Brit. Pat., 120081).—An alkylene or hydroxy-alkylene monohalogen-hydrin, for instance, ethylene or glycerol monochlorohydrin, is heated in water with *p*-acetylaminophenol or a substitution derivative thereof, in the presence of an equivalent quantity of alkali to combine with the halogen hydracid. For instance, 151 parts of *p*-acetylaminophenol are dissolved in an exactly equivalent quantity of 2*N*-sodium hydroxide solution, while cooling and shaking, and 81 parts of ethylene chlorohydrin are added; the mixture is heated at 60—70° for eight hours, and the β-hydroxyethyl ether separates as an oil, which crystallises on cooling. The yield is 85—90% of the theoretical, and the substance is purified by crystallising from hot water with treatment with animal charcoal. [See also *J. Soc. Chem. Ind.*, 1919, Jan.] J. F. B.

Transformation of Arylhydroxylamines into Aminophenols. F. KLAUS and O. BAUDISCH (*Ber.*, 1918, **51**, 1228—1230).—Finely powdered 3-*p*-toluenesulphonylmethylaminophenylhydroxylamine is added to a mixture of concentrated sulphuric acid and ice, water is added, and the whole is heated first on the water-bath and finally over a naked flame; the solution is filtered, neutralised with sodium carbonate, and sodium acetate is added, whereby 2-p-*toluenesulphonylmethylamino-4-aminophenol*,

$$NH_2\cdot C_6H_3(OH)\cdot NMe\cdot SO_2\cdot C_7H_7,$$

m. p. 163—164°, is obtained. It develops a violet coloration with ferric chloride, reduces ammoniacal silver oxide solution, and after diazotisation couples with phenols.

In a similar manner *o*-hydroxylaminophenyl *p*-toluenesulphonate is converted into 2-*amino-5-hydroxyphenyl* p-*toluenesulphonate*, which is obtained in the form of the *sulphate*, colourless crystals, m. p. 162°; the *hydrochloride* forms colourless needles, m. p. 187—190°. C. S.

A Compound of Strontium Bromide and Sodium Benzoate in Galenical Pharmacy. E. CANALS and J. SERRE (*Schweiz. Apoth. Zeit.*, **56**, 318—319; from *Chem. Zentr.*, 1918, ii, 468).

—*Strontium benzoate*, $(PhCO_2)_2Sr,3H_2O$, is obtained in small, transparent, hygroscopic needles, m. p. 410°, by mixing solutions of sodium bromide (20 grams), strontium bromide (20 grams), and sodium benzoate (12 grams), each dissolved in water (50 c.c.), diluting the mixture with an additional 150 c.c. of water, and allowing it to remain for twenty-four hours; the product is repeatedly crystallised from small quantities of hot water. At 15°, 1 part of the salt dissolves in 25·9 parts of water. H. W.

Basic Zirconyl Benzoates and Salicylates. F. P. VENABLE and F. R. BLAYLOCK (*J. Amer. Chem. Soc.*, 1918, **40**, 1746—1748).—The salts were prepared by precipitating a hot aqueous solution of zirconyl chloride with a similar solution of benzoic acid and subsequent washing with hot water. Analyses of different samples of the benzoate appear to show that under varying conditions as to concentration, etc., no single definite compound is formed. The precipitates have varying ratios between the acid radicle and the partly dehydrated zirconium hydroxide. The salicylates are notably less stable; they turn brown at 100° and become black at 160°. They appear to exhibit a tendency to form only one basic compound, in spite of varying conditions of formation, showing therein a difference from the precipitates formed with benzoic acid. H. W.

Preparation of 4-Sulphoaminobenzene-2-carboxylic [6-Amino-*m*-sulphobenzoic] Acid. FARBENFABRIKEN VORM. F. BAYER & Co. (D.R.-P. 307284, additional to D.R.-P. 296941; from *Chem. Zentr.*, 1918, ii, 574).—6-Amino-*m*-sulphobenzoic acid is conveniently prepared by the action of molecular amounts of chlorosulphonic acid and anthranilic acid dissolved in sulphuric acid monohydrate. The mixture is slowly heated to 90—100°, and subsequently to 130—140° after evolution of hydrogen chloride has ceased. Under these conditions, the monohydrate has practically no sulphonating action. H. W.

Citral Series. Condensation of Citral with Acetoacetic Ester. E. KNOEVENAGEL [with PAUL SEHLER, WILHELM STÖTZNER, RUDOLF STEINLE, GUSTAV MECHTERSHEIMER, WILHELM MAMONTOFF, and ADOLF STANG] (*J. pr. Chem.*, 1918, [ii], **97**, 288—335).—Five isomeric ethyl citrylideneacetoacetates have been obtained, the constitution of none of which has yet been definitely determined.

Ethyl citrylideneacetoacetate (α-ester), probably

$$CMe_2{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CMe{:}CH{\cdot}CH{:}CAc{\cdot}CO_2Et,$$

a pale yellow, faintly odorous liquid, b. p. 186°/12 mm., D_4^{19} 1·0202, D_4^{70} 0·9835, n_D^{19} 1·50645, is obtained by adding 72 drops of piperidine to a mixture of equal molecular quantities of ethyl acetoacetate and citral at about −15°, and keeping in the cold for about forty-eight hours. It changes partly to the β-ester (below) by repeated distillation or by prolonged exposure to light, dissolves easily in aqueous sodium hydrogen sulphite (therefore a double linking is

adjacent to a carbonyl group), and forms an oily *hydrobromide*, which is converted by boiling sodium carbonate solution into *ethyl* α-iso*citrylideneacetoacetate* (*terpinolenylacetoacetate*). This ester, which probably has the constitution $\mathrm{CMe}{\lessgtr}\begin{matrix}\mathrm{CH_2{\cdot}CHX}\\ \mathrm{CH{-}CH_2}\end{matrix}{>}\mathrm{C{:}CMe_2}$ or $\mathrm{CMe}{<}\begin{matrix}\mathrm{CH{\cdot}CHX}\\ \mathrm{CH_2{-}CH_2}\end{matrix}{>}\mathrm{C{:}CMe_2}$ (where $\mathrm{X=CHAc{\cdot}CO_2Et}$), forms colourless, rhombic plates, m. p. 69°, b. p. 164°/12 mm., D_4^{70} 1·0056, and is also obtained by heating the α-ester with a few c.c. of 30% sulphuric acid on the water-bath. By the addition of hydrogen bromide to the α-*iso*ester and its removal again by sodium carbonate, the α-*iso*ester is regenerated. The α-*iso*ester is difficultly hydrolysed, but is converted into α-iso*citrylideneacetoacetic* (*terpinolenylacetoacetic*) *acid*, crystals, m. p. 175° (with evolution of carbon dioxide), by alcoholic potassium hydroxide at 150°, or by very concentrated, boiling aqueous potassium hydroxide. The acid, the silver salt of which reacts with ethyl iodide to form the α-*iso*ester, is converted by heating at 180° into α-iso*ionone* (*terpinolenylacetone*), $C_{13}H_{20}O$, a faintly yellow oil, b. p. 122°/23 mm., D_4^{22} 0·9500, n_D^{22} 1·5021 (*semicarbazone*, colourless crystals, m. p. 205° [decomp.]), and is converted by 10% potassium permanganate and a slight excess of sodium carbonate below 3° into a saturated *acid*, $C_{14}H_{24}O_5$, crystals, m. p. 192°, but yields, when a little more permanganate is used, an *acid*, $C_{12}H_{22}O_4$, needles, m. p. 183·5°. The latter acid is converted by boiling water into a *substance*, $C_{12}H_{20}O_3$, m. p. 111° (p-*bromophenylhydrazone*, m. p. 174°), and by heating in a vacuum into an isomeric *substance*, m. p. 94°, b. p. 180°/23 mm., which changes into the substance, m. p. 111°, by keeping. The oxidation of the α-*iso*ester by chromic and acetic acids below 3° yields a *substance*, $C_{13}H_{18}O_4$, m. p. 42°, which forms a *semicarbazone*, yellowish-white needles, m. p. 193°. α-*iso*Ionone is oxidised by the preceding reagent to a *substance*, $C_{12}H_{18}O_3$, b. p. 168—171°/22·5 mm., m. p. 58°.

Ethyl citrylideneacetoacetate (β-ester), obtained by the repeated distillation of the α-ester in a vacuum and heating the product for eight hours at about 180° in a vacuum, or at about 230°/atm., has b. p. 168°/12 mm., D_4^{20} 1·0329, n_D^{20} 1·5072, and is insoluble in alkali hydrogen sulphite. Its formula is probably

$$\mathrm{CMe_2{:}CH{\cdot}CH_2{\cdot}CH{:}CMe{\cdot}CH{:}CH{\cdot}CHAc{\cdot}CO_2Et}.$$

It is hydrolysed by boiling concentrated aqueous potassium hydroxide, yielding β-ψ-*citrylideneacetoacetic acid*, probably

$$\begin{array}{l}\mathrm{CMe{\cdot}CH_2{\cdot}CH{\cdot}CH{:}CMe_2}\\ \Vert \qquad\qquad\quad \vert \\ \mathrm{CH{-}CH_2{\cdot}CAc{\cdot}CO_2H}\end{array},$$

crystals, m. p. 138° (decomp.), which by esterification by alcohol and 25% sulphuric acid at about 60° yields *ethyl* β-ψ-*citrylideneacetoacetate*, $C_{16}H_{24}O_3$, crystals, m. p. 99—100°, from which the β-ψ-acid is regenerated by hydrolysis. By oxidation with alkaline 1% permanganate (6 atoms of oxygen) below 5°, the β-ψ-acid yields an unsaturated *acid*, $C_8H_{12}O_3$, probably γ-*methyl*-Δ^{β}-*butenylpyruvic*

[*ε-methyl-Δ^δ-hepten-α-onoic*] *acid*, $CMe_2\colon CH\cdot CH_2\cdot CH_2\cdot CO\cdot CO_2H$, needles, m. p. 192° (decomp.), which reduces warm ammoniacal silver oxide solution. By heating above its m. p., the β-ψ-acid loses carbon dioxide and yields *β-ψ-ionone*, probably

$$\begin{array}{l} CMe\cdot CH_2\cdot CH\cdot CH\colon CMe_2 \\ CH-CH_2\cdot CHAc \end{array},$$

b. p. 125°/19 mm., D_4^{17} 0·9594, D_4^{22} 0·9547, n_D^{17} 1·49785 (*semicarbazone*, m. p. 152°).

The β-ester forms a *hydrobromide*, $C_{16}H_{25}O_3Br$, crystals, m. p. 93—94°, and is converted by heating with zinc chloride at 180° into *β-ionene*, $C_{13}H_{18}$, an oil with a characteristic odour, b. p. 63°/12 mm., D_4^{20} 0·8619, n_D^{20} 1·4904. The preceding hydrobromide is converted by boiling aqueous sodium carbonate into *ethyl β-isocitrylideneacetoacetate*, probably

$$CMe_2\colon CH\cdot CH_2\cdot CH_2\cdot CMe{<}{\begin{array}{c}CH\colon CH\\ CH_2\cdot CO\end{array}}{>}CH\cdot CO_2Et,$$

b. p. 160—161°/12 mm., D_4^{20} 1·0397, n_D^{20} 1·5082, which is insoluble in alkali hydrogen sulphite, regenerates the preceding hydrobromide, and by hydrolysis with boiling concentrated potassium hydroxide solution yields β-iso*citrylideneacetoacetic acid*, $C_{14}H_{20}O_3$, colourless crystals, m. p. 153°. This acid, the silver salt of which reacts with ethyl iodide to form the β-*iso*ester, is converted by heating at about 160° into β-iso*ionone*, probably

$$CH_2{<}{\begin{array}{c}CH\colon CH\\ CO\cdot CH_2\end{array}}{>}CMe\cdot CH_2\cdot CH_2\cdot CH\colon CMe_2,$$

b. p. 113°/15 mm., D_4^{20} 0·9481, n_D^{20} 1·4929, which forms a *semicarbazone*, crystals, m. p. 108°, and p-*bromophenylhydrazone*, crystals, m. p. 150—152°.

The reaction between citral and ethyl acetoacetate (2 mols.) below 0° in the presence of a little piperidine yields *ethyl citrylidenebisacetoacetate*,

$$CMe_2\colon CH\cdot CH_2\cdot CH_2\cdot CMe\colon CH\cdot CH(CHAc\cdot CO_2Et)_2,$$

colourless crystals, m. p. 64°, which forms an *oxime*, $C_{22}H_{35}O_6N$, crystals, m. p. 164°, and is converted by boiling alcoholic potassium hydroxide into 1-*methyl*-5-*β*ζ-*dimethyl*-Δ^αε-*heptadienyl*-Δ¹-cyclo*hexen*-3-*one*, $C_9H_{15}\cdot CH{<}{\begin{array}{c}CH_2-CO\\ CH_2\cdot CMe\end{array}}{>}CH$, b. p. 197—198°/15 mm., D_4^{20} 0·933, $D_4^{16\cdot5}$ 0·932, n_D^{20} 1·50846. The last compound is reduced by sodium and warm alcohol to the corresponding cyclo*hexanol*, $C_{16}H_{28}O$, b. p. 163—164°/11 mm., $D_4^{18\cdot5}$ 0·900, $n_D^{18\cdot5}$ 1·49182, which is oxidised by chromic acid to the corresponding cyclo*hexanone*, $C_{16}H_{26}O$, b. p. 172°/15 mm., $D_4^{18\cdot5}$ 0·907, $n_D^{18\cdot5}$ 1·49163, and is converted by phosphoric oxide at 190° into the cyclo*hexene*, $C_{16}H_{26}$, b. p. 143—144°/15 mm., $D_4^{18\cdot5}$ 0·923, $n_D^{18\cdot5}$ 1·4988. C. S.

Naphthylacetic Acids. III. 1-Nitro-β-naphthylpyruvic Acid and 1-Nitro-β-naphthylacetic Acid. FRITZ MAYER and TRUDI OPPENHEIMER (*Ber.*, 1918, **51**, 1239—1245. Compare A., 1918, i, 339).—1-Nitro-β-naphthylpyruvic acid is oxidised by

alkaline potassium permanganate to 1-*nitro-β-naphthaldehyde*, leaflets, m. p. 99° (small yield), and a *nitronaphthoic acid*, m. p. 239°, which is not identical with any of those described by Ekkestrand in 1885. The acid, which is also obtained by oxidising 1-nitro-β-naphthylpyruvic acid by bromine in alkaline solution, yields Friedländer and Littner's 1-amino-β-naphthoic acid, m. p. 202—205°, by reduction with ferrous sulphate and hot aqueous ammonia.

1-Nitro-β-naphthylpyruvic acid is reduced to α-naphthindole-2-carboxylic acid, m. p. 213° (Schlieper gives 202°), by ferrous sulphate and aqueous ammonia or by sodium amalgam, and is converted by hot dilute hydrochloric acid and sodium nitrite (1 mol.) into a *substance*, m. p. 131°, which appears to be 1-*nitro-β-naphthylacetonitrile*, $NO_2 \cdot C_{10}H_6 \cdot CH_2 \cdot CN$. By treatment with dilute aqueous sodium hydroxide and subsequent distillation with steam, 1-nitro-β-naphthylpyruvic acid yields, in addition to a little nitromethylnaphthalene, a substance the bisulphite compound of which gives α-naphthisatin when decomposed by boiling dilute sulphuric acid, and 1-*nitro-β-naphthylacetaldehyde*,

$$NO_2 \cdot C_{10}H_6 \cdot CH_2 \cdot CHO,$$

m. p. 212°, by treatment with dilute sulphuric acid in the cold. The last substance reacts with phenylhydrazine to form a *phenylhydrazone*, m. p. 162°, which appears to have the formula $NO_2 \cdot C_{10}H_6 \cdot CH(OH) \cdot CH{:}N \cdot NHPh$, since it contains an additional atom of oxygen.

1-Nitro-β-naphthylacetic acid is reduced to α-naphthoxindole by ferrous sulphate and aqueous ammonia. C. S.

Synthesis of Derivatives of Diethylaminoacetylsalicylic [o-Diethylaminoacetoxybenzoic] Acid. Friedrich L. Hahn and Milly Loos (*Ber.*, 1918, **51**, 1436—1447).—The following compounds have been prepared partly to obtain substances possessing certain advantages over aspirin and partly to ascertain how the presence of substituents in the acetoxy-group affects the stability of this group. With regard to the second point, the stability appears to be increased by substituents which weaken the acidity of the acetyl group.

Methyl o-*chloroacetoxybenzoate*, $CH_2Cl \cdot CO \cdot O \cdot C_6H_4 \cdot CO_2Me$, m. p. 62°, b. p. 195—200°/30 mm., prepared from methyl salicylate, chloroacetyl chloride, and dimethylaniline in the cold, is converted by sodium iodide in acetone solution into the corresponding *iodo-compound*, which in cold ethereal solution reacts with diethylamine to form, after treatment of the product in ethyl acetate solution with hydrogen chloride (not an excess), the *hydrochloride*, m. p. 131°, of *methyl* o-*diethylaminoacetoxybenzoate*,

$$NEt_2 \cdot CH_2 \cdot CO \cdot O \cdot C_6H_4 \cdot CO_2Me,$$

crystals, m. p. 58—59° (*picrate*, crystals, m. p. 147°). The *ethyl ester*, $C_{15}H_{21}O_4N$, b. p. 136—146°/11 mm., prepared from *ethyl* o-*chloroacetoxybenzoate*, m. p. 67°, b. p. 130°/25 mm., forms a *picrate*, needles, m. p. 138°, and *platinichloride*, m. p. 161—162°.

Diethylamine reacts with methyl *o*-chloroacetoxybenzoate to form methyl salicylate and *diethylaminoacetodiethylamide*,

$$NEt_2 \cdot CH_2 \cdot CO \cdot NEt_2$$

(*picrate*, crystals, m. p. 133°), and with chloroacetyl chloride in ether at 0° to form *chloroacetodiethylamide*, $CH_2Cl \cdot CO \cdot NEt_2$, b. p. 190—195°/25 mm. The last compound is converted into the corresponding *iodo*-compound, which reacts with ethereal diethylamine to form diethylaminoacetodiethylamide.

o-*Chloroacetoxybenzoyl chloride*, m. p. 55°, b. p. 165—170°/12 mm., prepared from the acid and phosphorus pentachloride and phosphoryl chloride, is converted into the *anilide*, m. p. 121°, and the latter into o-*iodoacetoxybenzanilide*, colourless crystals, m. p. 128°, which reacts with diethylamine in ethyl acetate solution to form o-*diethylaminoacetoxybenzanilide*, m. p. 129—130° (*hydrochloride*, m. p. 131—133°).

o-*Chloroacetoxybenzamide*, colourless needles, m. p. 160°, is obtained from *o*-chloroacetoxybenzoyl chloride and ammonium carbonate or ethereal ammonia, or from salicylamide and chloroacetyl chloride in the presence of dimethylaniline. o-*chloroacetoxybenzochloroacetamide*, $CH_2Cl \cdot CO \cdot O \cdot C_6H_4 \cdot CO \cdot NH \cdot CO \cdot CH_2Cl$, colourless needles, m. p. 133—134°, being an intermediate product in the last method of preparation. o-*Iodoacetoxybenzamide* has decomp. 138—139°.

o-*Diethylaminoacetoxybenzamide*, crystals containing $\frac{1}{2}H_2O$, m. p. 144—145°, forms a *hydrochloride*, m. p. 195—196°, which reacts with sodium nitrite in cold concentrated aqueous solution to form a substance, m. p. about 110°, which is apparently the impure *nitrite*. C. S.

Reduction of Methyl Formylphenylacetate to Methyl Tropate. WILHELM WISLICENUS and ERNST A. BILHUBER (*Ber.*, 1918, **51**, 1237—1238).—An ethereal solution of methyl formylphenylacetate is reduced by aluminium amalgam and water (compare Müller, A., 1918, i, 223), whereby *methyl tropate*, $C_{10}H_{12}O_3$, colourless needles, m. p. 36·5—37·5°, b. p. 159—162°/19 mm., is obtained, which yields tropic acid, m. p. 117—118°, by hydrolysis. C. S.

Action of Phosphorus Pentachloride on Formylphenylacetic Ester. WILHELM WISLICENUS and ERNST A. BILHUBER (*Ber.*, 1918, **51**, 1366—1371).—Börner (*Diss.*, Würzburg, 1899) and Koltscharsch (*Diss.*, Würzburg, 1901) have shown that ethyl formylphenylacetate (liquid α-ester) behaves as a true aldehyde, not as a hydroxymethylene compound, towards phosphorus pentachloride, yielding impure ethyl ββ-dichloro-α-phenylpropionate. A purer product is obtained from the α-methyl ester. *Methyl ββ-dichloro-α-phenylpropionate*, $CHCl_2 \cdot CHPh \cdot CO_2Me$, has b. p. 137—141°/23 mm., yields β-chloro-α-phenylacrylic (chloroatropic) acid by boiling with water, and is converted by alcoholic sodium methoxide into *methyl ββ-dimethoxy-α-phenylpropionate*, $C_{12}H_{16}O_4$, m. p. 46—47°, b. p. 135—142°/13 mm. C. S.

Studies in the Phenylsuccinic Acid Series. VII. The Action of Alcohols and Amines on *r*-Diphenylsuccinic Anhydride. HENRY WREN and HOWELL WILLIAMS (T., 1918, **113**, 832—840).

Preparation of a Calcium Tannate Sparingly Soluble in Dilute Acids. KNOLL & Co. (D.R.-P. 306979 and 307857; from *Chem. Zentr.*, 1918, ii, 494, 694).—If basic calcium tannate is heated for some time at a high temperature, it becomes sparingly soluble in dilute acids; a preparation which had been heated for six hours at 140—150° had the composition $Ca(OH)C_{14}H_9O_4$, and is recommended for treatment of dysentery.

The modification described in the second patent consists in heating solutions of tannic acid with the quantity of calcium hydroxide necessary for the production of the desired basic salt until the requisite sparing solubility of the basic calcium tannate in dilute acids is attained. H. W.

The Reaction between Acid Haloids and Aldehydes. ROGER ADAMS and E. H. VOLLWEILER (*J. Amer. Chem. Soc.*, 1918, **40**, 1732—1746).—The action of benzoyl bromide, of benzoyl chloride and a number of its substitution products, and of oxalyl bromide on aromatic aldehydes has been studied. The general method was to allow the mixtures to remain at the ordinary temperature until solidification occurred, a solvent, however, being occasionally used, more particularly in conjunction with oxalyl bromide. The substances obtained proved to be halogen-substituted esters of the general formula R·CHX·O·COR, or

R·CHX·O·CO·CO·O·CHXR

if oxalyl haloids had been used. They are all decomposed by water into aldehyde, organic acid, and halogen acid, but the difference in the rate of decomposition is very marked; thus, the compound from benzoyl bromide and anisaldehyde decomposes within a few seconds in moist air, whilst the nitrobenzoyl chlorides form compounds which are stable for a long time in cold water. The further reactions and the constitution of these compounds have been studied mainly at the instance of α-bromobenzyl benzoate (from benzoyl bromide and benzaldehyde). This compound is slowly decomposed by cold alcohol, yielding benzaldehyde, hydrogen bromide, and ethyl benzoate, and by an ethereal solution of ammonia, giving benzamide, benzaldehyde, and ammonium bromide; with aniline in dry ethereal solution, it yields α-bromobenzylaniline and benzoic acid. Its constitution follows from its conversion into benzylidene dibenzoate by the action of silver benzoate.

Benzoyl bromide has been condensed with the following aldehydes, the m. p.'s of the *products* being placed within brackets: *o*-bromobenzaldehyde (106—107°); *p*-bromobenzaldehyde (110°); nitroanisaldehyde (101—102°); acetylvanillin (102—103°); *p*-nitrobenzaldehyde (89—90°); bromopiperonal (108—113°); with

vanillin or salicylaldehyde, a vigorous action occurred, but the hydroxy-group was attacked; anisaldehyde (oily); with terephthalaldehyde, a pure product was not obtained; with piperonal, methylsalicylaldehyde, and methylvanillin the products were too unstable to permit purification.

Bromovanillin methyl ether and bromopiperonal react with benzoyl chloride, yielding *substances*, m. p.'s 158—160° and 97—102° respectively, whilst the crystals from benzaldehyde and *o*-, *m*-, and *p*-nitrobenzoyl chlorides have the respective m. p.'s 81—82°, 87—88°, 118—118·5°. Solid substances could not be obtained from benzaldehyde and *p*-chlorobenzoyl chloride, *p*-bromobenzoyl bromide, or *o*-bromobenzoyl chloride.

Oxalyl bromide has been allowed to react with the following aldehydes: benzaldehyde (130—131°); *o*-bromobenzaldehyde (140°); cinnamaldehyde (85—86°); anisaldehyde (ca 66° [decomp.]); nitroanisaldehyde (116—118°); *m*-nitrobenzaldehyde (128—129°); piperonal (81—83°); vanillin (93—95°); acetylvanillin (142—143°); furfuraldehyde (76—77°). Reaction was not observed with *p*-nitrobenzaldehyde.

α-Bromobenzyl benzoate yielded benzylidene dibenzoate, m. p. 62—63°, with silver benzoate, and *benzylidene acetate benzoate*, m. p. 71—72°, with silver acetate; similarly, *benzylidene benzoate* p-*nitrobenzoate*, m. p. 65—67°, was prepared from α-chloro-*p*-nitrobenzyl benzoate and silver benzoate.

α-Bromobenzyl benzoate reacted with *o*-toluidine in the same manner as with aniline, yielding *benzylidene-*o*-toluidine*, b. p. 210—212°/72 mm. With dimethylaniline, much heat was developed and a green, resinous product resulted. H. W.

αε-Dialdehydes and αε-Keto-aldehydes and their Conversion into δ-Lactones. Constitution and Method of Formation of Amaric Acid, Diethylcarbobenzonic Acid and Allied Compounds. HANS MEERWEIN (*J. pr. Chem.*, 1918, [ii], **97**, 225—287).—αε-Dialdehydes and αε-keto-aldehydes, of which glutardialdehyde is the only member hitherto known, are easily prepared by the two methods represented by the equations:

(1) $CH_2Ph{\cdot}COPh + CHR{:}CH{\cdot}CHO = COPh{\cdot}CHPh{\cdot}CHR{\cdot}CH_2{\cdot}CHO$,
(2*a*) $CH_2Ph{\cdot}CHO + CHR{:}CH{\cdot}CHO = CHO{\cdot}CHPh{\cdot}CHR{\cdot}CH_2{\cdot}CHO$,
and
(2*b*) $CH_2Ph{\cdot}CHO + CHR{:}CH{\cdot}COR' = CHO{\cdot}CHPh{\cdot}CHR{\cdot}CH_2{\cdot}COR'$.

Method (1) is new, and noteworthy in that it has hitherto been regarded as impossible to effect the addition of a compound containing a reactive methylene group at the double linking of an αβ-unsaturated aldehyde; yet in some cases the reaction proceeds with astonishing ease (see below). Satisfactory yields of the additive products are obtained by method (2), despite the well-known sensitiveness of phenylacetaldehyde towards alkali; the conclusion must therefore be drawn that the aldehydo-group causes a greater activation of the methylene hydrogen than does the acetyl or carboalkyloxy-group.

The constitutions of the keto-aldehydes described below are proved by oxidising the substances to the δ-ketonic acids, and all of them except ethyl α-acetyl-γ-aldehydo-βγ-diphenylbutyrate are converted by alcoholic sodium ethoxide into isomeric δ-lactones by an intramolecular Cannizzaro reaction. The stability of the δ-lactones and of the δ-hydroxy-acids obtained from them differs greatly. The α-mono- and αα-di-alkylated δ-hydroxy-acids are the most stable and lactonise comparatively slowly, and the fission of the corresponding lactones is the most difficult. The lactones almost without exception occur in stereoisomeric forms, which are very easily converted one into another by acids and alkalis. Three of the lactones prove to be the long-known diethylcarbobenzonic acid, dipropylcarbobenzonic acid, and amaric anhydride, and the mechanism of the formation of these substances is now readily explicable.

The type of additive reaction represented in method (1) suggests a new explanation of the formation of benzanthrone from anthrone, glycerol, and sulphuric acid, depending on the structural similarity of anthrone and deoxybenzoin. Acraldehyde is formed, and this reacts additively with anthrone, producing β-anthronylpropionaldehyde, which passes through dihydrobenzanthrone to benzanthrone.

[With Jos. Klinz.]—*β-Phenyl-β-desylpropaldehyde*,

$$COPh\cdot CHPh\cdot CHPh\cdot CH_2\cdot CHO,$$

needles, m. p. 176·5—177° (when heated slowly, decomp.), obtained with the development of heat by the addition of 1—2 c.c. of concentrated sodium methoxide solution or pyridine or diethylamine to a solution of equal molecular quantities of cinnamaldehyde and deoxybenzoin in methyl alcohol at about 5°, yields β-phenyl-β-desylpropionic (Klingemann's β-dehydroamaric, A., 1893, 589) acid by oxidation with chromic or nitric and glacial acetic acids, and is converted into βγδ-triphenylvalerolactone (Zinin's amaric anhydride) by boiling anhydrous sodium methoxide solution, and into δ-hydroxy-βγδ-triphenylvaleric (α-amaric) acid by aqueous methyl-alcoholic potassium hydroxide at the ordinary temperature, more rapidly by warming. The constitution of β-phenyl-β-desylpropionic acid has been proved by its synthesis. Methyl benzylidenemalonate and deoxybenzoin, condensed as above, yield the additive *compound*, $COPh\cdot CHPh\cdot CHPh\cdot CH(CO_2Me)_2$, needles, m. p. 182·5—183°, which by hydrolysis and loss of carbon dioxide is converted into β-phenyl-β-desylpropionic acid, m. p. 240—241°. Klingemann's dehydroamaric anhydride is accordingly the lactone, $\begin{array}{l} CHPh\cdot CH_2\cdot CO \\ | \qquad\qquad\quad | \\ CPh{:}CPh-O \end{array}$. The reduction of β-phenyl-β-desylpropionic acid by sodium amalgam yields an acid which changes very readily into *β-amarolactone*, $C_{23}H_{20}O_2$, prismatic needles, m. p. 168—170°, from which *β-amaric acid*, $C_{23}H_{22}O_3$, needles (reconverted into the lactone at 156°), is obtained in the usual way. Since β-amaric acid regenerates β-phenyl-β-desylpropionic acid by oxidation, the α- and β-amaric acids are stereoisomerides.

The substance, $C_{11}H_{18}O_2$, m. p. 168°, obtained by Klingemann by heating α-amarolactone (amaric anhydride) with 25% alcoholic sulphuric acid at 100° (*loc. cit.*), is now found to be a third isomeride, $C_{23}H_{20}O_2$, m. p. 171—172°, which is named γ-*amarolactone*. By oxidation with chromic and acetic acids, it yields an isomeric β-phenyl-β-desylpropionic acid, needles, m. p. 173°, which is much more soluble than the acid, m. p. 240—241°, is converted into this by fusion, and is identical with Klingemann's α-dehydroamaric acid.

The additive compound of deoxybenzoin and α-methyl-β-ethylacraldehyde is an oil, which doubtless consists essentially of β-*desyl-α-methylvaleraldehyde*, COPh·CHPh·CHEt·CHMe·CHO, since it yields β-*desyl-α-methyl*-n-*valeric acid*, m. p. 141·5—143°, by oxidation. It has not been obtained crystalline, and decomposes completely by distillation in a vacuum. By treatment in concentrated methyl-alcoholic solution at 30—40° with a few c.c. of sodium methoxide solution, it is converted into γδ-diphenyl-α-methyl-β-ethylvalerolactone, m. p. 152°, which is identical with Zagoumenny's dipropylcarbobenzonic acid. The corresponding *hydroxy-acid*, $C_{20}H_{24}O_3$, forms prismatic needles, m. p. 136—137° (decomp.). Zagoumenny's dipropylcarbobenzonic acid, m. p. 139°, is shown to be a mixture of the β-acid, m. p. 92—93°, and the preceding acid, m. p. 152°, which is called the α-acid. The α-acid is converted into the β-acid by heating with methyl-alcoholic potassium hydroxide at 160° for five hours. The β-acid is dimorphous, crystallising also in needles, m. p. 95—96°. By oxidation with chromic and acetic acids, the α- and β-acids yield respectively β-desyl-α-methyl-*n*-valeric acid and an isomeric *acid*, $C_{20}H_{22}O_3$, prismatic needles, m. p. 184·5—185°. A third *isomeride*, needles, m. p. 169—171°, is obtained by acidifying a solution of the *sodium* salt, leaflets, of the β-desyl-α-methyl-*n*-valeric acid, m. p. 141·5—143°. By reduction with sodium amalgam, the acid, m. p. 141·5—143°, yields, not α-dipropylcarbobenzonic acid, but a mixture of two other stereoisomerides, γ-*dipropylcarbobenzonic acid* [γ-(γδ-*diphenyl-α-methyl-β-ethylvalerolactone*)], needles, m. p. 82—84°, and δ-*dipropylcarbobenzonic acid* [δ-(γδ-*diphenyl-α-methyl-β-ethylvalerolactone*)], needles, m. p. 134°, softening at 130°, of which the latter is insoluble in light petroleum.

The additive compound of crotonaldehyde and deoxybenzoin is β-*desylbutaldehyde*, COPh·CHPh·CHMe·CH_2·CHO, which yields β-*desyl*-n-*butyric acid*, needles, m. p. 134—136°, by oxidation. The latter is converted into an *isomeride*, m. p. 153·5—154·5°, by 2% aqueous sodium hydroxide at 50—60°. A synthesis of β-desylbutyric acid, m. p. 134—136°, from deoxybenzoin and ethylidenemalonic ester, analogous to that of β-phenyl-β-desylpropionic acid (above), is described. β-Desylbutaldehyde in methyl-alcoholic solution is transformed by aqueous potassium hydroxide into γδ-diphenyl-β-methylvalerolactone, m. p. 103—104°, which is identical with Zagoumenny's diethylcarbobenzonic acid (the α-acid). By oxidation with chromic and acetic acids, the α-acid

yields β-desyl-*n*-butyric acid, m. p. 134—136°, but the latter on reduction yields *β-diethylcarbobenzonic acid* [(β)-γδ-*diphenyl-β-methylvalerolactone*], needles, m. p. 144—146°. The oxidation of the β-acid yields the β-desyl-*n*-butyric acid, m. p. 153·5—154·5°, from which it would appear that the β-acid is formed by the reduction (by sodium amalgam), not of the β-desyl-*n*-butyric acid, m. p. 134—136°, but of the isomeric acid, m. p. 153·5—154·5°, so easily obtained from it by the action of alkali hydroxide.

Deoxybenzoin and acraldehyde react additively in methyl-alcoholic solution containing a little sodium methoxide to form *β-desylpropaldehyde*, which yields β-desylpropionic acid by oxidation. The aldehyde cannot be transformed by alkali into *γδ-diphenylvalerolactone*, $C_{17}H_{16}O_2$, needles, m. p. 113—114°, which is obtained, however, by the reduction of β-desylpropionic acid by sodium-amalgam.

[With HANS DOTT.]—The additive reaction between phenylacetaldehyde and cinnamaldehyde in cold methyl-alcoholic sodium methoxide solution yields αβ-diphenylglutardialdehyde. This has not been isolated from the solution, but converted by heating on the water-bath into *βγ-diphenylvalerolactone*, prisms or needles, m. p. 123—123·5°, together with a small quantity of a *substance*, m. p. 134—136°, leaflets, which is possibly αβ-diphenylvalerolactone. By oxidation with alkaline permanganate, βγ-diphenylvalerolactone yields *αβ-diphenylglutaric acid*, prisms, m. p. 203—204° (*methyl ester*, needles, m. p. 84—85°), which is converted by prolonged fusion into a stereoisomeride (methyl ester, prisms, m. p. 143°), m. p. between 215° and 232°, according to the rate of heating. For this isomeride Borsche found m. p. 230—231° (A., 1910, i, 35), and Avery and McDole m. p. 223—224° (A., 1908, i, 343). By reduction with hydriodic acid (D 1·7) and red phosphorus at 170°, βγ-diphenylvalerolactone yields *βγ-diphenyl-n-valeric acid*, prismatic needles, m. p. 109°, the constitution of which follows by exclusion, since the acid is not identical with either of the stereoisomeric forms of αβ-diphenylvaleric acid.

δ-Keto-αβδ-triphenyl-*n*-valeraldehyde, obtained additively from phenylacetaldehyde and phenyl styryl ketone, has also not been isolated, but has been converted through αβδ-triphenylvalerolactone into *δ-hydroxy-αβδ-triphenylvaleric acid*, needles, m. p. 143—143·5°, which is a remarkably stable acid, but is converted into *αβδ-triphenylvalerolactone*, needles, m. p. 138—139°, by heating in a vacuum at 150°. The acid is oxidised by chromic acid or potassium permanganate, although not smoothly, to *δ-keto-αβδ-triphenylvaleric acid*, which is best isolated as the *methyl* ester, $C_{24}H_{22}O_3$, needles, m. p. 157—158°. The acid, felted needles, m. p. 186—187°, has been obtained by hydrolysing the ester and also synthetically from phenyl styryl ketone and methyl phenylacetate. A second isomeric *acid* is also obtained by the synthetic method, which has m. p. 260—261°, forms a *methyl* ester, needles, m. p. 177—178°, and is also obtained by heating the acid, m. p. 186—

187°, at 200—220°. $\alpha\beta\delta$-Triphenylvalerolactone is reduced to *$\alpha\beta\delta$-triphenylvaleric acid*, m. p. 174—175°, by hydriodic acid (D 1·7) and red phosphorus at 170°, and is converted by warm glacial acetic acid containing 10% of sulphuric acid into a *stereoisomeride*, $C_{23}H_{20}O_2$, prisms with $1C_2H_4O_2$, m. p. 124° (174° after removal of acetic acid), from which is obtained a *δ-hydroxy-$\alpha\beta\delta$-triphenylvaleric acid*, prisms with 1EtOH, m. p. 155° (not sharp), with reconversion into the lactone.

Phenylacetaldehyde and ethyl benzylideneacetoacetate react additively in alcoholic solution at 5° in the presence of a little sodium ethoxide to form *δ-keto-γ-carbethoxy-$\alpha\beta$-diphenylhexaldehyde*, CHO·CHPh·CHPh·CHAc·CO_2Et, rhombic leaflets containing $1H_2O$, m. p. 149° (decomp.), and a *substance*, $C_{23}H_{28}O_5$, prisms, m. p. 79—81°. This substance, the constitution of which has not yet been determined, is also formed by treating the aldehyde with 5% alcoholic hydrogen chloride; it is converted by distillation in a vacuum into an unsaturated *substance*, $C_{23}H_{26}O_4$, needles, m. p. 129—130°. The preceding aldehyde, which is a viscous oil in the anhydrous state, is converted by distillation in a vacuum into ethyl acetoacetate and *α-phenylcinnamaldehyde*, crystals, m. p. 94° (*oxime*, leaflets, m. p. 165—166°; *phenylhydrazone*, yellow needles, m. p. 125—126°), which has also been synthesised from phenylacetaldehyde and benzaldehyde by Claisen's method.

[With Jos. Klinz.]—*Methyl β-anthronyl-β-phenylisosuccinate*, $CO<\substack{C_6H_4\\C_6H_4}>CH\cdot CHPh\cdot CH(CO_2Me)_2$, prisms, m. p. 147°, prepared by adding a few drops of piperidine or diethylamine to a warm methyl-alcoholic solution of anthrone and methyl benzylidenemalonate, is converted into *β-anthronyl-β-phenylpropionic acid*, prisms, m. p. 195—197° (rapidly heated; decomp. by slow heating), by hydrolysis with boiling 30% sulphuric and glacial acetic acids for four to five days.

By similar additive reactions, anthrone unites with ethyl benzylideneacetoacetate and with phenyl styryl ketone to form *ethyl α-acetyl-β-anthronyl-β-phenylpropionate*,

$$CO<\substack{C_6H_4\\C_6H_4}>CH\cdot CHPh\cdot CHAc\cdot CO_2Et,$$

needles, m. p. 148—149°, and *phenyl β-anthronyl-β-phenylethyl ketone*, $CO<\substack{C_6H_4\\C_6H_4}>CH\cdot CHPh\cdot CH_2\cdot COPh$, needles, m. p. 115—116°, respectively. C. S.

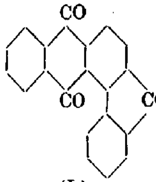
Action of Potassium Ferricyanide on Alizarin in Alkaline Solution and Constitution of Salts of Hydroxyanthraquinones. Roland Scholl and A. Zinke (*Ber.*, 1918, **51**, 1419—1435).—By oxidation with an aqueous solution of potassium

ferricyanide and potassium hydroxide at the ordinary temperature, alizarin is converted into an *acid*, $C_{14}H_8O_6$, hydrated, yellow leaflets, m. p. about 230° (decomp.; darkening above 150°), which is purified through the *calcium* salt, and the *monoethyl* ester, yellow or brownish-yellow crystals, m. p. 149°, or *diethyl* esters, yellow plates, prisms, or needles, m. p. 85·5—87°, and yellow, prismatic needles, m. p. 188° (probably *cis-trans*-isomerides). The acid is shown to be 2-*hydroxy*-1 : 4-*naphthaquinone*-3-*vinylglyoxylic acid*, $OH\cdot C_{10}H_4O_2\cdot CH\colon CH\cdot CO\cdot CO_2H$, by the following evidence. It acts as a dibasic acid, forming a calcium salt, $C_{14}H_6O_6Ca$, which exists in four forms, violet-brown crystals with $7H_2O$, blackish-violet crystals with $3H_2O$, blackish-violet salt with $1H_2O$, and bronze, rhombic leaflets with $2H_2O$, and a *dipotassium* salt, $C_{14}H_6O_6K_2$, brown crystals with $2H_2O$. It forms a vat with alkaline hyposulphite, and therefore contains a quinone grouping. It can be converted into a naphthafuranquinone, and is therefore a naphthaquinone derivative. The monoethyl ester gives a violet-red coloration with alcoholic ferric chloride. The acid reacts additively with bromine.

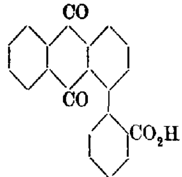
The views of Perkin (T., 1899, **75**, 433; 1903, **83**, 129), von Georgievics (A., 1902, i, 635; 1905, i, 447), Werner (A., 1908, i, 440), Pfeiffer (A., 1913, i, 879), and Dimroth (*Annalen*, 1916, **411**, 340) on the constitution of hydroxyanthraquinones in the form of their salts and the nature of mordant dyes are discussed without any very definite conclusion being reached. C. S.

Rearrangement Reactions in the Anthraquinonefluorenone Series. ALFRED SCHAARSCHMIDT and JOHANN HERZENBERG (*Ber.*, 1918, **51**, 1230—1237).—1-Chloroanthraquinone-2-carboxylic acid is converted by boiling with toluene and phosphorus pentachloride into the acid *chloride*, pale yellow needles, a suspension of which in benzene is converted into 1-*chloro*-2-*benzoylanthraquinone*, $C_{21}H_{11}O_3Cl$, yellow leaflets, m. p. 196°, by heating with aluminium chloride at 60° for four hours. 1-*Amino*-2-*benzoylanthraquinone*, red needles, m. p. 190°, prepared by heating the preceding substance with alcohol and aqueous ammonia at 170—175°, is diazotised in concentrated sulphuric acid solution at 17—22°, the solution is poured on to ice so that the temperature does not exceed about 35°, copper powder is added, and the mixture warmed on the water-bath, whereby *anthraquinone*-2 : 1-*fluorenone* (formula I), golden-yellow leaflets (from nitrobenzene), m. p. 317°, is obtained, which forms an intensely red vat with sodium hyposulphite. By fusion with potassium hydroxide at 220—230°, anthraquinone-2 : 1-fluorenone is converted, not into 1-o-carboxyphenylanthraquinone (formula II) as might be expected from the behaviour of allochrysoketonecarboxylic acid (Schaarschmidt, A., 1917, i, 274), but into a mixture of acids containing the dicarboxylic acid (formula III), since by treatment with concentrated sulphuric

acid, Ullmann and Dasgupta's anthraquinone-2:3-fluorenone (A., 1914, i, 413) was obtained (formula IV).



(I.)



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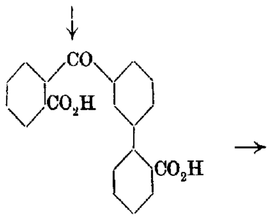

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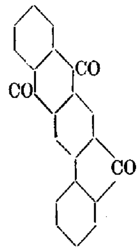


(IV.)

C. S.

Camphor Ketones. HANS RUPE, MARKUS WARDER, and KUNIHIKO TAKAGI (*Helv. Chim. Acta*, 1918, i, 309—342).—The work of Rupe and Iselin (A., 1916, i, 409) and of Rupe and Burckhardt (A., 1917, i, 141) on the preparation of derivatives of methylenecamphor has been extended in several directions, particularly with a view to the preparation of an unsaturated camphor ketone; the optical investigation of the substances is not yet quite completed, and fuller details are promised in a subsequent communication.

Camphorylideneacetic acid, $C_8H_{14}<\begin{matrix}C{=}CH\cdot CO_2H\\ |\\ CO\end{matrix}$, m. p. 99·5—101°, $[\alpha]_D$ +182·3° in benzene, is prepared by a modification of the method of Bishop, Claisen, and Sinclair (A., 1895, i, 62) [the microcrystalline *magnesium* salt and the ethyl *ester*, pale yellow, inodorous oil, b. p. 149·5—150°/12 mm., D_4^{20} 1·0459, $[\alpha]_D$ +170·1° (in substance), +160·4 (in benzene), are described], and is converted by thionyl chloride into the corresponding *chloride*, m. p. 34—35°, b. p. 140—141°/13 mm. The free acid reacts with hydrogen bromide in glacial acetic acid solution, yielding the bromo-*acid*,

$$C_8H_{14}<\begin{matrix}CBr\cdot CH_2\cdot CO_2H\\ |\\ CO\end{matrix},$$

long, colourless needles, m. p. 153—154° (decomp.), but the action appears to be balanced, since, at a slightly higher temperature, hydrogen bromide is eliminated with re-formation of camphorylideneacetic acid. The latter substance does not react normally with bromine. *Camphorylacetic acid*, small, prismatic crystals, m. p. 83—84°, b. p. 191·5—192·5°/12 mm., $[\alpha]_D$ +38·0 in benzene, is prepared by reducing camphorylideneacetic acid with sodium amalgam, or, better, with hydrogen, in the presence of nickel; its *ethyl ester* has b. p. 154—155°/10 mm., $[\alpha]_D$ +67·5° (in substance), +37·1° (in benzene). Attempts to reduce camphorylideneacetyl chloride by zinc dust and acetic acid led to the isolation of a mixed *anhydride* of camphorylacetic and acetic acids, $C_8H_{14}<\begin{matrix}CH\cdot CH_2\cdot CO\cdot O\cdot Ac\\ |\\ CO\end{matrix}$, fine needles or transparent plates, m. p. 118—120°.

Ethyl dicamphorylideneacetylmalonate,

$$\left(C_8H_{14}<\begin{matrix}C{=}CH\cdot CO\\ |\\ CO\end{matrix}\right)_2 C(CO_2Et)_2,$$

pale yellow needles, m. p. 90—91°, is prepared by the condensation of camphorylideneacetyl chloride with ethyl sodiomalonate in ethereal solution (*ethyl dicamphorylideneacetylacetoacetate*, fine needles, m. p. 149—150°, is similarly obtained from ethyl acetoacetate), and is hydrolysed by dilute sulphuric acid in acetic acid solution to *camphorylideneacetone*, $C_8H_{14}<\begin{matrix}C{=}CH\cdot CO\cdot CH_3\\ |\\ CO\end{matrix}$, lemon-yellow liquid, b. p. 137—138°/10 mm., D_4^{20} 1·0327, $[\alpha]_D$ +208·8° (in substance), 186·6° (in benzene), and camphorylideneacetic acid. The ketone does not appear to yield a stable sodium hydrogen sulphite compound; the *benzylidene* derivative forms golden-yellow needles, m. p. 94—95°, p-*nitrobenzylidene* derivative, lemon-yellow, minute crystals, m. p. 150—151°, *oxime*, colourless, shining needles, m. p. 142—143°, *phenylhydrazone*, orange-yellow needles, m. p. 145—146°, *hydrazone*, long, yellow needles, m. p. 112—113°. With semicarbazide the ketone gives a *compound*, $C_{14}H_{21}O_2N_3$, prismatic needles or small leaflets, decomposing at 223—224°, which does not behave as a normal semicarbazone.

Attempts to prepare *camphorylacetone* by a similar sequence of actions were less successful. *Camphorylacetyl chloride*, pale yellow, inodorous liquid, b. p. 152—154°/12 mm., could only be condensed with ethyl sodiomalonate with considerable difficulty, giving a small yield of substance, from which by hydrolysis camphorylacetone was obtained in small quantity. The saturated ketone could, however, be satisfactorily prepared by reduction of camphorylideneacetone with hydrogen in the presence of nickel, although the camphor carbonyl group was invariably attacked to some extent; after purification through the *semicarbazone*, long needles, m. p. 203—204° (decomp.), it was obtained as an inodorous, highly refractive oil, b. p. 148·5—149°/12 mm., D_4^{20} 1·0213, $[\alpha]_D$ +49·2° (in substance), +60·7° (in benzene). The ketone behaves towards sodium hydrogen sulphite in the same manner as the unsaturated ketone; it yields a

phenylhydrazone, needles, m. p. 87—89°, and a *benzylidene* derivative, colourless leaflets, m. p. 75—76°.

The preparation of a camphordiketone is also described, although the yields leave much to be desired in spite of many variations of the experimental conditions; ethyl camphorylacetate condenses with acetophenone in ethereal solution in the presence of solid sodium ethoxide, giving small amounts of *camphorylacetylacetophenone*, $C_8H_{14}<\begin{matrix}CH\cdot CH_2\cdot CO\cdot CH_2\cdot COPh\\ |\\ CO\end{matrix}$, m. p. 59—61°, $[\alpha]_D$ +62·5° in benzene. An alcoholic solution of the diketone gives an immediate bluish-red coloration with ferric chloride. The *copper* salt, long, greyish-green needles, m. p. 184—186°, and *sodium* salt are described. H. W.

Preparation of Camphylcarbinol. HANS RUPE (D.R.-P. 307357; from *Chem. Zentr.*, 1918, ii, 493).—Hydroxymethylenecamphor only suffers reduction at the ethylenic bond when reduced by hydrogen in the presence of finely divided nickel or cobalt in alcoholic, aqueous-alcoholic, or acetic acid solution, or as normal alkali salt in aqueous solution; *camphylcarbinol*, which is thus produced, is a colourless, odourless oil, b. p. 142—143°/10 mm., D_4^{20} 1·0502, $[\alpha]_D^{20}$ +62·22°. [See further, following abstract.] H. W.

Reduction Products of Hydroxymethylenecamphor. H. RUPE, A. AKERMANN, and H. TAKAGI (*Helv. Chim. Acta.*, 1918, **1**, 452—472).—The reduction of hydroxymethylene compounds by hydrogen in the presence of colloidal palladium or platinum has been studied by Kötz and Schaeffer (A., 1912, i, 603), who found that methyl ketones were formed; hydroxymethylenecamphor, however, was unaffected by this treatment, a result which was attributed to the acidic character of the substance. The authors find that hydroxymethylenecamphor is readily reduced by hydrogen in the presence of a specially prepared nickel catalyst (the mode of procedure is fully described in the original paper and iron and copper are shown to act as poisons). The main product (about 80—95%) of the reaction is *camphylcarbinol*, $C_8H_{14}<\begin{matrix}CH\cdot CH_2\cdot OH\\ |\\ CO\end{matrix}$; it is purified by repeated fractionation under diminished pressure, or, preferably, by means of the calcium chloride *compound*; the optically pure substance is isolated through the benzoyl derivative (see later). It forms a colourless, odourless, viscous oil, b. p. 139—140°/9 mm., 143—144°/11 mm., D_4^{20} 1·0502, $[\alpha]_C^{20}$ +49·13°, $[\alpha]_D^{20}$ +65·73°, $[\alpha]_E^{20}$ +82·44°, $[\alpha]_F^{20}$ +120·82°, $[\alpha]_F/[\alpha]_C$ 2·45°, $\lambda\alpha$ 578. With phosphorus tribromide it yields the corresponding *bromide*, long needles, m. p. 65·5—66°, and with hydrogen chloride, or, preferably, thionyl chloride, the corresponding *chloride*, leaflets, m. p. 53—54°, b. p. 125—127°/14 mm. Attempts to convert the alcohol into the aldehyde were unsuccessful; chromic oxide converted it into camphorquinone, m. p. 197°, whilst manganese dioxide and sulphuric

acid gave a small quantity of substance, m. p. 201°, and much unchanged carbinol. Benzoyl chloride in the presence of pyridine converts the carbinol practically quantitatively into the *benzoyl* derivative, colourless, shining plates or prisms, m. p. 95—97°; attempts to hydrolyse the latter with alcoholic potassium hydroxide, with barium hydroxide, or magnesia resulted in the formation of methylenecamphor. Experiments with aqueous alcoholic sulphuric acid were more successful, and from these it was found possible to isolate camphylcarbinol, although dehydration of the latter also occurred to a considerable extent. The *formyl* derivative, long needles, m. p. 74—75°, b. p. 142—143°/11 mm., and the *acetyl* derivative, colourless, mobile oil, b. p. 148·5—149°/10 mm., were prepared by the action of formic acid (86%) and acetic anhydride respectively on the carbinol, but attempts to prepare the hydrogen phthalate led to the production of methylenecamphor.

The by-products of the preparation of camphylcarbinol consist of methylenecamphor, methylcamphor, and the ethyl ethers of camphylcarbinol and hydroxymethylenecamphor. The two substances first named are contained in the first fractions, b. p. *ca.* 82—84°/10 mm., and are separated by converting the methylenecamphor into the hydrobromide (camphylbromomethane), from which it can be re-generated by treatment with methyl-alcoholic potassium hydroxide; the pure substance is, however, more conveniently prepared by heating camphylcarbinol with the same reagent, and then forms a characteristic, waxy mass, m. p. 43·5—44°. It becomes polymerised when repeatedly distilled under diminished pressure. With bromine it yields a *dibromide*, m. p. 108—109°. *Methylcamphor*, $C_8H_{14}<\begin{matrix}CHMe\\ | \\ CO\end{matrix}$, can be isolated in an almost pure state by repeated fractionation of the residues from the methylenecamphor hydrobromide, but is more conveniently obtained by the direct hydrogenation of methylenecamphor in the presence of finely divided nickel; it has m. p. 37·5—38·5°, b. p. 88—89°/8·5 mm. Direct experiment shows the formation of methylenecamphor to be due to the dehydrating action of the nickel catalyst on primarily formed camphylcarbinol.

The ethyl ethers of camphylcarbinol and hydroxymethylenecamphor were not isolated as such; their presence is inferred from the fact that the action of alcoholic potassium hydroxide on the fractions of higher b. p. of the by-products leads to the production of methylenecamphor and hydroxymethylenecamphor respectively; their formation is attributed to the addition of ethyl alcohol to methylenecamphor and to the condensation of hydroxymethylenecamphor and alcohol under the influence of nickel. H. W.

Synthesis of Curcumin. V. LAMPE (*Ber.*, 1918, 51, 1347—1355).—The course of the synthesis is as follows: ethyl α-carbomethoxyferuloylacetoacetate ⟶ carbomethoxyferuloylacetone ⟶ dicarbomethoxydiferuloylacetone ⟶ dicarbomethoxydiferuloylmethane ⟶ diferuloylmethane (curcumin).

Ethyl α-carbomethoxyferuloylacetoacetate [*ethyl α-4-methylcarbonato-3-methoxycinnamoylacetoacetate*],

$$CO_2Me\cdot O\cdot C_6H_3(OMe)\cdot CH{:}CH\cdot CO\cdot CHAc\cdot CO_2Et,$$

obtained by digesting ethyl sodioacetoacetate and carbomethoxyferuloyl [4-methylcarbonato-3-methoxycinnamoyl] chloride in dry ether on the water-bath, forms faintly yellow needles, m. p. 91—93°; a by-product of the reaction is *methyl carbonatomethoxycinnamic anhydride*, $C_{24}H_{22}O_{11}$, colourless leaflets, m. p. 142—144°. *Ethyl α-feruloylacetoacetate*, $C_{16}H_{18}O_6$, canary-yellow, prismatic needles, m. p. 116—118°, is obtained by shaking an ethereal solution of the methyl carbonato-derivative with 1% aqueous sodium hydroxide and treating the alkaline solution with carbon dioxide.

Carbomethoxyferuloylacetone [*4-methylcarbonato-3-methoxycinnamoylacetone*], $CO_2Me\cdot O\cdot C_6H_3(OMe)\cdot CH{:}CH\cdot CO\cdot CH_2\cdot COMe$, faintly yellow, prismatic needles, m. p. 111—113°, is obtained by hydrolysing ethyl α-methylcarbonatomethoxycinnamoylacetoacetate, carbon dioxide being also eliminated; it is converted into *feruloylacetone*, $C_{13}H_{14}O_4$, prisms, m. p. 143—145°, by dilute alkali.

A solution of methylcarbonatomethoxycinnamoylacetone in anisole is treated with finely divided sodium, and a day later a solution of methylcarbonatomethoxycinnamoyl chloride in warm anisole is added. The mixture is treated after twenty-four hours with water containing a little hydrochloric acid, and the anisole is removed by distillation with steam. The heavy, dark red residue, probably dimethylcarbonatomethoxydicinnamoylacetone, is boiled with dilute acetic acid, and thus converted into dimethylcarbonatomethoxydicinnamoylmethane, m. p. 145—148—158°; after crystallisation from benzene the substance is pure, has m. p. 170—172°, and is identical with Milobendzka, Kostanecki, and Lampe's dimethylcarbonatocurcumin (A., 1910, i, 628); the last substance has m. p. 170—172° after being crystallised from benzene. On hydrolysis dimethylcarbonatomethoxydicinnamoylmethane yields diferuloylmethane, $CH_2(CO\cdot CH{:}CH\cdot C_6H_3[OMe]\cdot OH)_2$, prisms, m. p. 180—183°, which is identical with natural curcumin. C. S.

Synthesis of *pp'*-Dihydroxy- and *p*-Hydroxydicinnamoylmethane. V. Lampe and M. Godlewska (*Ber.*, 1918, **51**, 1355—1360).—The method of synthesising dicinnamoylmethane (Lampe and Milobedzka, A., 1913, i, 876) has been extended to include the hydroxy-derivatives, partly in connexion with the synthesis of curcumin (preceding abstract), partly to obtain substances which are of interest in connexion with the theory of direct dyes.

The condensation of ethyl acetoacetate and *p*-methylcarbonatocinnamoyl chloride in ethereal solution by means of sodium ethoxide yields, in addition to a little p-*methylcarbonatocinnamic anhydride*, $C_{22}H_{18}O_9$, colourless aggregates, m. p. 168—170°, *ethyl α-p-methylcarbonatocinnamoylacetoacetate*,

$$CO_2Me\cdot O\cdot C_6H_4\cdot CH{:}CH\cdot CO\cdot CHAc\cdot CO_2Et,$$

faintly yellow prisms, m. p. 94—96°, which yields by hydrolysis and simultaneous elimination of carbon dioxide p-*methylcarbonatocin-*

namoylacetone, $CO_2Me·O·C_6H_4·CH:CH·CO·CH_2·COMe$, faintly yellow leaflets, m. p. 111—113°. The last compound reacts in ethereal solution with very dilute alkali to form p-*hydroxycinnamoylacetone*, yellow leaflets, m. p. 144—146°, in boiling alcoholic solution with hydroxylamine hydrochloride to form 3(or 5)-p-*methylcarbonatostyryl*-5(or 3)-*methyl*isoo*xazole*, $C_{14}H_{13}O_4N$, colourless leaflets, m. p. 122—124°, and in anisole solution with sodium and *p*-methylcarbonatocinnamoyl chloride to form, after the initial product has been boiled with dilute acetic acid (compare preceding abstract), pp′-*dimethylcarbonatodicinnamoylmethane*, $C_{23}H_{20}O_8$, canary-yellow aggregates, m. p. 162—166°. The last substance reacts with hydroxylamine hydrochloride in alcoholic solution to form 3:5-*di*-p-*methylcarbonatostyryl*isoo*xazole*, $C_{23}H_{19}O_7N$, colourless aggregates, m. p. 178—180°, and in ethereal solution with 1% aqueous sodium hydroxide to form pp′-*dihydroxydicinnamoylmethane*, $C_{19}H_{16}O_4$, faintly orange needles, m. p. 218—220° (decomp.).

p-*Methylcarbonatodicinnamoylmethane*, $C_{21}H_{18}O_5$, yellow needles, m. p. 114—116°, is obtained from cinnamoylacetone and *p*-methylcarbonatocinnamoyl chloride or *p*-methylcarbonatocinnamoylacetone and cinnamoyl chloride by the aid of sodium and acetic acid (as above), and yields by elimination of the carbomethoxy-group p-*hydroxydicinnamoylmethane*, faintly orange, prismatic needles, m. p. 190—192°.

Unmordanted cotton is dyed faintly orange by curcumin, canary-yellow (not fast to soap) by *pp′*-dihydroxydicinnamoylmethane, and faintly yellow by *p*-hydroxydicinnamoylmethane. A similar regularity occurs in the reaction with boric acid, which colours turmeric (curcumin) paper intensely orange, changes the colour of *pp′*-dihydroxydicinnamoylmethane to a weak orange, and does not affect the colour of *p*-hydroxydicinnamoylmethane. C. S.

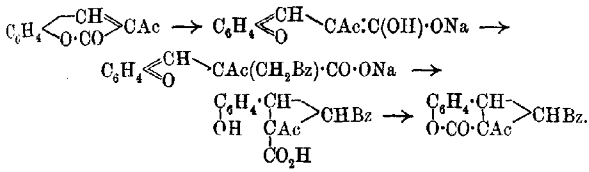
A New Group of *cyclo*Propane Derivatives. III. Scope and Mechanism of the Reaction. Behaviour of 3-Acetylcoumarin with Solutions of Alkali Hydroxides. OSKAR WIDMAN (*Ber.*, 1918, **51**, 1210—1214. Compare A., 1918, i, 347, 393).—The formation of the new *cyclo*propane derivatives by the reaction:

$$R·CO·CH_2Cl + C_6H_4\left\langle\begin{matrix}CH:CR' \\ O—CO\end{matrix}\right. = \left.\begin{matrix}C_6H_4–CH \\ O·CO·CR'\end{matrix}\right\rangle CH·COR + HCl$$

(*loc. cit.*) succeeds when R = Ph, *o*- or *p*-$C_6H_4·OMe$, $C_6H_4·NO_2$, or $C_{10}H_7$ and R′ = Ac, COEt, Bz, CO_2Et, CO_2Me, or CN, but fails when R = Me and R′ = Ph or H. The formation also fails when ethyl coumarin-4-carboxylate is used instead of a suitably 3-substituted coumarin. Attempts also failed to bring about, in the presence of sodium ethoxide, a reaction between phenacyl haloids and esters of fumaric, ethylenetetracarboxylic, benzylideneacetoacetic, benzylidenemalonic, anisylidenemalonic, and *o*-ethoxybenzylideneacetoacetic acids in such a way that the phenacylidene group is combined at a double linking. It appears, therefore, that only 3-substituted coumarins can enter into the preceding reaction, and even then only

if the substituent is an aliphatic or aromatic acyl group, a carbo-alkyloxy-group, or a cyano-group.

In seeking to account for the reaction, the author has revised his explanation of the action of alkalis on 3-acetylcoumarin (A., 1902, i, 374). The yellow colour developed with a cold solution of alkali hydroxide is now attributed, not to the formation of 3-hydroxyvinyl-coumarin, because 3-trimethylacetyl- and 3-benzoyl-coumarin, in which the formation of the hydroxyvinyl group is impossible, also develop a yellow colour, but to the formation of an orthoquinonoid sodium compound. This reacts with the phenacyl haloid in accordance with the scheme:



When alcoholic sodium ethoxide is used a certain amount of the substance $O{:}C_6H_4{:}CH\cdot CAc{:}C(OEt)\cdot ONa$ is formed, and this reacts with the phenacyl haloid to yield the coumarinic ester,

$$OH\cdot C_6H_4\cdot CH<\begin{matrix}CHBz\\ |\\ CAc\cdot CO_2Et\end{matrix},$$

and thus is explained the formation of a by-product differing from the main product in containing an additional molecule of ethyl alcohol (*loc. cit.*). C. S.

A Synthesis of *iso*Brazilein and certain Related Anhydro-pyranol Salts. I. HERBERT GRACE CRABTREE, ROBERT ROBINSON, and MAURICE RUSSELL TURNER (T., 1918, **113**, 859—880).

Preparation of Hydrogenated Alkaloids. C. F. BOEHRINGER & SÖHNE (D.R.-P., 307894; additional to D.R.-P., 306939; from *Chem. Zentr.*, 1918, ii, 693—694).—The addition of hydrogen to alkaloids or their salts in the presence of small quantities of the finely divided suboxides of the nickel group (A., 1918, i, 546) at temperatures not exceeding 60° can also be effected in alcoholic suspension or solution. The preparation of dihydroquinine from quinine monohydrochloride and the hydrogenation of cinnamyl-cocaine are cited as examples. H. W.

Cinchona Alkaloids. I. Cupreine, Hydrocupreine, and their Methyl and Ethyl Ethers. G. GIEMSA and J. HALBERKANN (*Ber.*, 1918, **51**, 1325—1333).—Contrary to the statement of Hesse (A., 1888, 71), dihydrocupreine instantly decolorises potassium permanganate in acid solution. It has m. p. 204° (Hesse gives 168—170°; Pum, 170°), and can readily be obtained by the addition of hydrogen to cupreine in alcoholic solution (palladium catalyst) or to cupreine hydrochloride in aqueous solution (nickel catalyst).

Cupreine yields methylcupreine (quinine) by methylation with methyl sulphate and alkali in methyl-alcoholic solution, or, much better, with ethereal diazomethane in amyl-alcoholic solution.

Methyldihydrocupreine, prepared by the catalytic reduction of quinine or the methylation of dihydrocupreine, is isolated as the *basic sulphate*, which contains $6H_2O$ and is relatively stable to potassium permanganate. Ethyldihydrocupreine is prepared by similar methods. C. S.

The Cinchona Alkaloids. XX. Synthesis of Quinotoxines. PAUL RABE and KARL KINDLER (*Ber.*, 1918, **51**, 1360—1365. Compare A., 1918, i, 303).—The problem of the synthesis of quinotoxines resolves itself into three parts: (1) the synthesis of cinchoninic and 6-methoxycinchoninic acids, (2) the synthesis of homomeroquinene and homocincholeupone, and (3) the condensation of each of the first with each of the second pair to give the four quinotoxines, cinchonicine, dihydrocinchonicine, quinicine, and dihydroquinicine.

The first part will be dealt with in a later communication by Rabe. With regard to the second part, the two substances have not yet been synthesised, and the material used by the authors in realising the third part has been obtained by the fission of quinotoxines. Thus *N*-benzoylhomocincholeupone, obtained from benzoyldihydrocinchotoxine by a slight modification of Kaufmann and Brunnschweiler's method (A., 1917, i, 50), is converted into its *ethyl* ester, $C_{19}H_{27}O_3N$, a viscous oil, b. p. 256°/13 mm., which yields, after hydrolysis by dilute hydrochloric acid and subsequent re-esterification, *ethyl homocincholeupone*, $C_{12}H_{23}O_2N$, b. p. 140°/13 mm. The reaction between ethyl cinchoninate and ethyl *N*-benzoylhomocincholeupone in the presence of sodium ethoxide in boiling benzene for fifteen hours leads to a product, doubtless the β-ketonic ester,

$$NBz{<}{\substack{CH_2-CH_2\\ CH_2\cdot CHEt}}{>}CH\cdot CH_2\cdot CH(CO_2Et)\cdot CO\cdot C_9H_6N,$$

which is converted into dihydrocinchotoxine (dihydrocinchonicine) by hydrolysis with boiling 15% hydrochloric acid.

Since dihydrocinchotoxine can be converted into dihydrocinchoninone (A., 1909, i, 253), and the latter has been reduced by aluminium and sodium ethoxide to dihydrocinchonine and dihydrocinchonidine (future communication), therefore the construction of cinchona alkaloids from derivatives of the quinoline and piperidine series has been accomplished. C. S.

Degradation of Scopoline. ERNST SCHMIDT (*Ber.*, 1918, **51**, 1281—1283).—A claim for priority over Hess with respect to the conversion of dihydroscopoline into 1-methylpiperidine-2:6-dicarboxylic acid, and a denial of his statement (A., 1918, i, 404) that the author has asserted that the group $O{<}{\substack{C(OH)\\ |\\ CH}}$ is present in scopoline. C. S.

Strychnine Alkaloids. XXIV. Cause of the Violet Colour Reaction of Cacotheline and of Nitro-compounds of the Brucine Series Allied to it. HERMANN LEUCHS (*Ber.*, 1918, 51, 1375—1389).—The action of nitric acid on brucine is represented by the scheme $C_{23}H_{26}O_4N_2 \longrightarrow C_{21}H_{20}O_4N_2 \longrightarrow C_{21}H_{19}O_6N_3 \longrightarrow C_{21}H_{21}O_7N_3,HNO_3$ (A., 1911, i, 746). Cacotheline, the final product, would appear to be a nitrated quinone were it not that sulphurous acid does not produce a less intensely coloured or colourless quinol (A., 1910, i, 1042), but a substance having a deep violet or deep green colour. Brucinolone and *iso*brucinolone when treated with nitric acid undergo analogous changes (A., 1909, i, 954; 1912, i, 210; 1913, i, 194), the final product being undoubtedly a nitroquinone, since it is reduced by sulphurous acid to a pale yellow quinol. Hence by analogy the cacotheline base is a nitro-quinone, despite the objection raised above. The same holds in the case of the methonitrate of the cacotheline base, $C_{21}H_{21}O_7N_3,MeNO_3$, obtained by the action of nitric acid on methylbrucine (A., 1911, i, 1018). The methonitrate also gives a violet coloration with sulphurous acid, but its quinonoid nature is shown first by the reaction with aqueous hydroxylamine hydrochloride, whereby the *oxime*, $C_{22}H_{25}O_7N_4Cl,2H_2O$, yellow needles, of the methochloride of the cacotheline base is obtained, and, secondly, by reduction by tin and *N*-hydrochloric acid, whereby four atoms of hydrogen are taken up and a *stannichloride*, broad, rectangular prisms, is obtained, $C_{22}H_{28}O_5N_3Cl,HCl,SnCl_4,6H_2O$, from which the *hydrochloride* of presumably an amino-quinol, $C_{22}H_{28}O_5N_3Cl,HCl,H_2O$, colourless, crystalline powder, decomp. 260°, is prepared. The behaviour of the methonitrate towards sulphurous acid is at variance with the preceding evidence of quinonoid structure. Thus with aqueous sodium hydrogen sulphite it yields, in the cold at 0°, a *methosulphite* of the cacotheline base,

$$C_{21}H_{21}O_7N_3,MeSO_3H,6H_2O,$$

colourless leaflets, which evolves sulphur dioxide on treatment with strong acids, and in the hot solution an isomeric *methosulphite*, deep violet, almost black prisms with metallic lustre (into which the colourless isomeride changes by keeping), which dissolves in concentrated sulphuric acid without evolution of sulphur dioxide, and is precipitated unchanged by the addition of water. Probably, therefore, the sulphurous acid in the violet compound is not only attached to the basic nitrogen atom, but also enters into complex combination with some other portion of the molecule. By treatment with 5*N*-nitric acid, the violet compound loses two atoms of hydrogen and is converted into a *substance*, $C_{21}H_{19}O_7N_3,MeSO_3H$, reddish-yellow leaflets or prisms with $2H_2O$, which appears to bear to the violet compound the relation of quinone to quinol, since it is converted into the latter by sulphurous acid or by nickel and hydrochloric acid. Hydroxylamine, however, converts the reddish-yellow substance into the violet compound in acid solution and into the oxime of the methochloride of the cacotheline base in alkaline solution. The complete reduction of the reddish-yellow

substance by tin and hydrochloric acid yields at first a violet precipitate, and, finally, a *substance*, $C_{22}H_{25}O_7N_3S$, colourless needles, which appears to be the anhydride resulting by the elimination of water from an amino- and the SO_3H-groups. The SO_2 group is still present in complex union in the anhydride, but is eliminated by warm *N*-alkali hydroxide, without, however, definite products being formed.

The violet compound, $C_{21}H_{21}O_7N_3,MeSO_3H$, is stable in aqueous ammonia in the absence of oxygen, but when the latter is admitted is oxidised, to the extent of 10% to the reddish-yellow nitroquinone methosulphite and to the extent of 60% to a *substance*, $C_{21}H_{23}O_{11}N_3S$, reddish-yellow prisms and polyhedra, carbonising at about 280—290°.

Apart from their acidic groups, the methonitrate of the cacotheline base, and the violet methosulphite obtained from it by the action of sodium hydrogen sulphite, are isomeric substances. The former is a nitro-quinone and the latter a nitro-quinol. The reduction of the one to the other is not effected at the expense of the sulphurous acid, because the two substances are isomeric. The author is of opinion that intramolecular reduction occurs at the expense of a ·CH(OH)· group in the cacotheline base, and that the resulting ·CO· group enters into complex union with the sulphite group; thus, (i) ·CO·CO· + :CH·OH ⟶ ·C(OH):C(OH)· + :CO, and (ii) :NMe·SO_3H + :CO ⟶ :NMe·SO_2·O·C(OH):. C. S.

Acid Esters of 2 : 6-Dimethylcinchomeronic Acid. RUD. WEGSCHEIDER (*Ber.*, 1918, **51**, 1478—1479).—Mumm and Hüneke's argument that the acid ester produced by the interaction of alcohol and the acid anhydride must be the γ-ester on steric grounds (A., 1918, i, 183) is inadmissible, because the author has shown frequently (1895—1912) that in reactions of this kind the alcohol attacks the strongest carboxyl group present, even though it may be sterically protected. C. S.

New Cases of Isomerism in the Isatin Series. II. GUSTAV HELLER (*Ber.*, 1918, **51**, 1270—1281).—The existence of 5 : 7-dimethylisatin (and also of four dimethyl ethers) in four modifications (A., 1918, i, 235) is now shown to be incorrect. 5 : 7-Dimethylisatin I is the lactam, $C_6H_2Me_2<\substack{CO\\NH}>CO$, since it exhibits all the reactions characteristic of isatin itself in the lactam form. The O-silver salt does not exist, the compound previously described as such being a complex substance containing very much more silver than the amount corresponding with the simple formula. The only silver derivative is the N-salt, and this reacts with methyl iodide in the presence of benzene at 100° to form the lactim ether, $C_6H_2Me_2<\substack{CO\\N}\geqslant C\cdot OMe$, m. p. 232°, which is identical with the previously described methyl ether of isomeride II (m. p. erroneously given as 247°). The sodium salt and methyl iodide yield the lactam ether.

Isomeride II.—This is produced from the isomeride I, has the ame composition, is unimolecular, gives the indophenin reaction, nd yields the preceding lactim ether by warming with methyl ulphate. It is therefore 5:7-dimethylisatin in the lactim form, which, unlike the corresponding form of isatin, is capable of isolated xistence.

The lactim methyl ether is converted into 5:7-dimethylisatin (lactam) by boiling glacial acetic acid or hot dilute aqueous sodium hydroxide.

Since 5:7-dimethylisatin can exist in the lactam and the lactim forms, its salts may be N- or O-salts. The silver and the sodium salts prepared from the lactam regenerate this on acidification, and are thus N-salts, and therefore by analogy the silver and the sodium salts of isatin itself are lactam salts. No evidence of the formation of O-salts has been obtained.

Isomeride III.—This is dimethylisatol, $C_6H_2Me_2{<}\overset{C(OH)}{\underset{N}{}}{>}CO$. Its methyl ether is converted in the lactim ether by heating with 50% acetic acid.

Isomeride IV.—This substance, in the purest form obtained, crystallises in red needles, m. p. about 315°, sintering above 285°. It appears to contain a different ring system, and it is regenerated when its methyl ether is heated with 50% acetic acid. C. S.

Action of Acylamino-acid Chlorides on Sodiomalonic sters. V. S. GABRIEL and BRUNO LÖWENBERG (*Ber.*, 1918, **51**, 193—1500).—o-*Phthaliminobenzoyl chloride*,

$$C_6H_4{<}^{CO}_{CO}{>}N{\cdot}C_6H_4{\cdot}COCl,$$

out prisms, m. p. 152—153°, prepared by heating *o*-phthalimino-enzoic acid with phosphorus pentachloride, reacts with a benzene spension of methyl sodiomalonate to form the yellow sodium erivative of *methyl* o-*phthaliminobenzoylmalonate*,

$$C_6H_4{<}^{CO}_{CO}{>}N{\cdot}C_6H_4{\cdot}CO{\cdot}CH(CO_2Me)_2,$$

it prisms, m. p. 159—161°. This substance, which is decom-osed into methyl iodide, carbon dioxide, phthalic acid, and aminoacetophenone by boiling hydriodic acid, does not resemble ie analogously constituted substances,

$$C_6H_4{<}^{CO}_{CO}{>}N{\cdot}CR_2{\cdot}CO{\cdot}CH(CO_2Me)_2$$

reviously described by Gabriel (1913—1915) in its behaviour with dium methoxide, since by treatment with a 4% methyl-alcoholic lution it yields, not the expected 6-ring analogue of the tetramic ids, but first the sodio-derivative, which then decomposes, yield-g *methyl* o-*phthaliminobenzoate*, stout crystals, m. p. 160—162° also prepared from *o*-phthaliminobenzoyl chloride and methyl-coholic sodium methoxide), and *methyl* 2-o-*carboxybenzoylamino-*

benzoate, $CO_2H\cdot C_6H_4\cdot CO\cdot NH\cdot C_6H_4\cdot CO_2Me$, flat leaflets, m. p. 145—146° (also prepared by heating together methyl anthranilate and phthalic anhydride). A second point of difference is the behaviour of the sodio-derivative on methylation, since by heating with methyl iodide and acetone at 100°, it yields, not a C-methyl derivative, but the O-*methyl* derivative,

$$C_6H_4{<}{}^{CO}_{CO}{>}N\cdot C_6H_4\cdot C(OMe)\colon C(CO_2Me)_2,$$

crystals, m. p. 148—149°, which is converted into phthalic and anthranilic acids by boiling hydrochloric or hydrobromic acid, but into methyl iodide, carbon dioxide, and a *substance*, $C_{17}H_{13}O_5N$, flat needles or plates, m. p. 248° (decomp.), by hydriodic acid; this substance, which is probably *4-keto-2-o-carboxyphenyl-1:2:3:4-tetrahydroquinoline-3-carboxylic acid*, yields carbon dioxide, aniline, and phthalidylacetic acid by heating at 180° with fuming hydrochloric acid.

Ethyl o-phthaliminobenzoylmalonate, $C_{22}H_{19}O_7N$, prisms, m. p. 101—107°, sintering at 94°, yields *ethyl o-phthaliminobenzoate*, stout prisms, m. p. 108—109°, and *ethyl 2-o-carboxybenzoylaminobenzoate*, needles, m. p. 114—116°, by treatment with sodium methoxide, and its sodio-derivative yields the O-*ethyl* derivative, $C_{24}H_{23}O_7N$, m. p. 89—90°, and O-*methyl* derivative, $C_{23}H_{21}O_7N$, prisms, m. p. 104—106°, from which the preceding dicarboxylic acid, $C_{17}H_{13}O_5N$, is obtained by the action of hydriodic acid.

C. S.

Some Quinoline Derivatives. S. GABRIEL (*Ber.*, 1918, **51**, 1500—1515. Compare preceding abstract).—Since *o*-phthaliminobenzoylmalonic esters yield *o*-aminoacetophenone by treatment with acids (*loc. cit.*), *o*-phthaliminobenzoylcyanoacetic esters have been prepared in the hope that they would yield *o*-amino-ω-cyanoacetophenone, from which a quinoline derivative could be prepared. These expectations have been fulfilled.

Ethyl sodiocyanoacetate and *o*-phthaliminobenzoyl chloride react in benzene to form the yellow *sodio*-derivative of *ethyl o-phthaliminobenzoylcyanoacetate*,

$$C_6H_4{<}{}^{CO}_{CO}{>}N\cdot C_6H_4\cdot CO\cdot CH(CN)\cdot CO_2Et,$$

flat needles, m. p. 178—179°. The latter forms an *ammonium* derivative, yellow prisms, and a *silver* derivative, $C_{20}H_{13}O_5N_2Ag$, from which methyl iodide and acetone at 100° produce a *methyl* derivative, crystals, m. p. 173—174°, which is probably the O-ether,

$C_6H_4{<}{}^{CO}_{CO}{>}N\cdot C_6H_4\cdot C(OMe)\colon C(CN)\cdot CO_2Et$, since it yields the substance, $C_9H_8ON_2$, (see below) by boiling with hydriodic acid.

When treated with *N*-alkali hydroxide in the cold, and then with hydrochloric acid, ethyl *o*-phthaliminobenzoylcyanoacetate yields the ester of a dibasic acid, probably

$$CO_2H\cdot C_6H_4\cdot CO\cdot NH\cdot C_6H_4\cdot CO\cdot CH(CN)\cdot CO_2Et,$$

microscopic prisms or crusts, m. p. 263—265° (decomp.; sintering above 255°), which develops a cherry-red coloration with ferric chloride, and is converted by glacial acetic acid with warming into phthalic acid and 3-*cyano*-2:4-*dihydroxyquinoline*, $C_{10}H_6O_2N_2$, colourless needles, m. p. above 300° (decomp.; sintering at about 270°); the last substance is converted into 2:4-dihydroxyquinoline by boiling hydriodic acid, and into 2:4-*dichloro*-3-*cyanoquinoline*, colourless needles, m. p. 168—169°, by boiling with phosphoryl chloride and phosphorus pentachloride for one and a-half hours. If the boiling proceeds for only half an hour, the product is 4(or 2)-*chloro*-3-*cyano*-2(or 4)-*hydroxyquinoline*, flat needles, not molten at 280°. The dichlorocyanoquinoline is converted into kynurenic acid by boiling hydriodic acid (b. p. 127°) and red phosphorus.

By boiling with hydrobromic or, better, hydriodic acid, ethyl *o*-phthaliminobenzoylcyanoacetate is converted into phthalic acid and a *substance*, $C_9H_8ON_2$, long needles with $1H_2O$ from water or anhydrous crystals from alcohol, m. p. about 303—304°, sintering at about 285°, which forms a *hydrobromide*, $C_9H_8ON_2,HBr$, slender needles, *platinichloride*, and *aurichloride*, and is proved to be 2-*amino*-4-*hydroxyquinoline*, the intermediately formed *o*-amino-ω-cyanoacetophenone not being isolated; a by-product of the reaction is 2:4-dihydroxyquinoline.

By treatment with nitric (D 1·30) and glacial acetic acids on the water-bath, 2:4-dihydroxyquinoline is converted into 3-*nitro*-2:4-*dihydroxyquinoline*, sulphur-yellow prisms, decomp. about 225°, which possesses pronounced acid properties and yields 2:4-*dichloro*-3-*nitroquinoline*, needles, m. p. 102°, by heating with phosphoryl chloride; the last substance is reduced to 3-aminoquinoline by tin and hydrochloric acid.

o-Nitrobenzoyl chloride reacts with ethyl sodiocyanoacetate in the presence of ether to form, after treatment of the initial product with hydrochloric acid, *ethyl o-nitrobenzoylcyanoacetate*, $NO_2\cdot C_6H_4\cdot CO\cdot CH(CN)\cdot CO_2Et$, needles, m. p. 91°, which is reduced and hydrolysed by boiling hydriodic acid and red phosphorus, yielding ethyl iodide, carbon dioxide, and 2-amino-4-hydroxyquinoline. The aminohydroxyquinoline is converted by very dilute hydrochloric acid and alkali nitrite (1 mol.) into the *iminoquinisatoxime*, $C_6H_4{<}\begin{matrix}NH\cdot C{:}NH\\ CO-C{:}N\cdot OH\end{matrix}$ or $C_6H_4{<}\begin{matrix}N{=}C\cdot NH_2\\ CO\cdot C{:}N\cdot OH\end{matrix}$, which forms a *potassium* salt, $C_9H_6O_2N_3K$, garnet-red needles, and a *hydrochloride*, $C_9H_7O_2N_3,HCl$, orange-yellow needles, yields 3-nitro-2:4-dihydroxyquinoline by warming with nitric acid (D 1·34), and is reduced by tin and 20% hydrochloric acid to the *hydrochloride*, colourless crystals containing $1H_2O$, of a *base*, $C_9H_8O_2N_2$, needles containing $1H_2O$, not molten at 300°, which is probably 2-amino-3:4-dihydroxyquinoline. By trituration with hydriodic acid (b. p. 127°), the iminoquinisatoxime is converted into 2:3-*diamino*-4-*hydroxyquinoline*, flat needles (*hydrochloride*, $C_9H_9ON_3,2HCl$, needles).

The reduction of quinisatoxime by hydriodic acid or by tin and

20% hydrochloric acid yields the *hydrochloride*, $C_9H_8O_2N_2,HCl,H_2O$, colourless needles, not molten at 285°, of 3-*amino*-2:4-*dihydroxyquinoline*, microscopic needles, not molten at 280°. The base, which is also obtained by reducing 3-nitro-2:4-dihydroxyquinoline by tin and hydrochloric acid, forms a *hydriodide*,

$$C_9H_8O_2N_2,HI,H_2O,$$

colourless needles, and an *acetyl* derivative, darkening above 200°, but not molten at 285°. C. S.

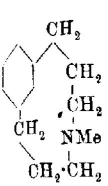
Bases of the Julolidine Type. J. VON BRAUN, KARL HEIDER, and WANDA WYCZATKOWSKA (*Ber.*, 1918, **51**, 1215—1227).—Such bases are of interest in connexion with the phenomena of steric hindrance in tertiary bases and the fission of hydrogenised indole and quinoline derivatives by sodium amalgam (von Braun, A., 1917, i, 282).

Lilolidine, $C_6H_3{<}\begin{matrix}CH_2\text{——}CH_2\\ CH_2\cdot CH_2\cdot CH_2\end{matrix}{>}N$ (compare Bamberger and Sternitzki, A., 1893, i, 520), b. p. 156°/15 mm., cannot be prepared from tetrahydroquinoline and ethylene dibromide, but is produced by gently boiling a mixture of dihydroindole (1 part) and γ-chloropropyl bromide (6 parts) for eighteen hours. It forms a *picrate*, m. p. 138°, and a *methiodide*, and resembles dimethylaniline in its behaviour towards formaldehyde, yielding a viscous diphenylmethane derivative, $CH_2(C_{11}H_{12}N)_2$, and towards benzaldehyde in the presence of zinc chloride, yielding ultimately an intensely green substance. The *methochloride* exhibits remarkable stability towards 5% sodium amalgam, the rings being unbroken and lilolidine being regenerated. This stability is in marked contrast to those of the methochlorides of tetrahydroquinoline and dihydroindole, in which the rings are ruptured to the extent of 60% and 25% respectively.

2-Methyldihydroindole and γ-chloropropyl bromide, boiled together for four to five hours, yield 2-*methyl*-1-γ-*chloropropyldihydroindole*, $C_{12}H_{16}NCl$, b. p. 172—175°/15 mm., but after eighteen hours 2-*methyl-lilolidine*, $C_6H_3{<}\begin{matrix}CH_2\text{——}CHMe\\ CH_2\cdot CH_2\cdot CH_2\end{matrix}{>}N$, is obtained, b. p. 165—167°/15 mm., which forms a *picrate*, m. p. 140°, and a *methiodide*, m. p. 202°, resembles lilolidine in its behaviour towards formaldehyde and benzaldehyde, and the *methochloride* of which is mainly unruptured by sodium amalgam, only about 10% of it being converted into a *base*, $C_{13}H_{19}N$, colourless oil, b. p. 151°/15 mm. (*picrate*, yellow needles, m. p. 121°; *platinichloride*, m. p. 177—178°). This base, which yields a *m*-diamine by nitration and subsequent reduction, must be 1:2-*dimethyl*-7-n-*propyldihydroindole*, because it is not identical with the only other substance possible, namely, 8-n-*propylkairoline*. The last-mentioned substance was synthesised as follows: *o*-Propylaniline, obtained from tetrahydroquinoline through *o*-γ-chloropropylbenzanilide, is converted by

the Skraup method into 8-*propylquinoline*, b. p. 142°/15 mm. (*platinichloride*, m. p. 196°; *picrate*, yellowish-red needles, m. p. 142°), the *methiodide*, m. p. 136°, of which is reduced by tin and hydrochloric acid to 8-n-*propylkairoline* (*picrate*, m. p. 108—109°; *platinichloride*, m. p. 164°).

Julolidine, prepared by Pinkus's method (A., 1892, 1491. For large quantities of materials the time of heating must be prolonged to eight hours to prevent the formation of halogenated impurities), resembles the lilolidines in its behaviour towards benzaldehyde and formaldehyde (the oily diphenylmethane derivative yields a *dimethiodide*, $C_{27}H_{36}N_2I_2$, colourless crystals, m. p. 228°), and forms a methiodide much more readily than does 8-methylkairoline or dimethyl-*o*-toluidine. The *methochloride* by reduction with 5% sodium amalgam yields 63% of julolidine and 37% of a *base*, $C_{13}H_{19}N$, b. p. 144—148°/23 mm. (*picrate*, yellow needles, m. p. 189°, decomposition beginning above 180°; *platinichloride*, m. p. 191°; *methiodide*, colourless crystals, m. p. 200°), which is not the expected 8-*n*-propylkairoline, but appears to have the annexed formula. It is remarkable in that it contains a 10-ring, and is a meta-bicyclic compound. It is a saturated substance, yields *iso*phthalic acid by oxidation with alkaline permanganate, does not condense with benzaldehyde to give ultimately a green colouring matter, does not yield a meta-diamine by nitration and subsequent reduction, and its methiodide, after treatment with silver oxide and distillation, yields a *base*, $C_{14}H_{21}N$, b. p. 117—118°/3 mm., which does not form crystalline salts, is unsaturated and is regarded as γ-3-*allylphenyl*-n-*propyldimethylamine*, $CH_2{:}CH{\cdot}CH_2{\cdot}C_6H_4{\cdot}[CH_2]_3{\cdot}NMe_2$.



C. S.

Proteinogenous Amines. I. Synthesis of β-Iminazolylethylamine [Histamine]. KARL K. KOESSLER and MILTON TH. HANKE (*J. Amer. Chem. Soc.*, 1918, **40**, 1716—1726).—The method followed is based on that of Pyman (T., 1911, **99**, 668), but several additions and improvements have been effected. Full descriptions are given of the preparation of acetonedicarboxylic acid, dioximinoacetone, diaminoacetone stannichloride, diaminoacetone hydrochloride, 2-thiol-4(or 5)-aminomethylglyoxaline hydrochloride, 4(or 5)-hydroxymethylglyoxaline picrate, 4(or 5)-hydroxymethylglyoxaline hydrochloride, and of iminazolylethylamine dichloride (histamine dichloride); the separation of methylglyoxaline and of glyoxalineacetic acid is also described. One hundred and sixty-five grams of histamine dichloride are obtained from 4530 grams of citric acid.

H. W.

Phenomena of Luminescence in Pyrazoline Derivatives. FRITZ STRAUS [with CARL MUFFAT and W. HEITZ] (*Ber.*, 1918, **51**, 1457—1477).—In consequence of the striking ease with which pyrazolines are obtained directly by the action of phenylhydrazine

on phenyl styryl ketone, distyryl ketone, and ethyl γ-keto-$\Delta^{\alpha\epsilon}$-pentadiene-$\alpha\epsilon$-dicarboxylate, the intermediary phenylhydrazones not being isolable, and of the phenomena of luminescence exhibited by these substances, the reaction has been extended to include a series of substituted ketones and substituted hydrazines. It is found that pyrazolines are formed except (1) when *p*-nitrophenylhydrazine is used, (2) when an *o*-methoxy-group is present in the phenyl group of the ketone, and (3) when the phenylhydrazine and a phenyl group of the ketone both contain a halogen substituent; in these three cases the phenylhydrazones or substituted phenylhydrazones are stable, and require special treatment for their conversion into pyrazolines.

The following substances are described. The method of von Auwers and Voss (A., 1910, i, 70), reduction by sodium amalgam with the formation of aniline, is used to distinguish the phenylhydrazones from the pyrazolines.

1-α-*Naphthyl-5-phenyl-3-styrylpyrazoline*, prepared from distyryl ketone and α-naphthylhydrazine in boiling alcohol, forms yellow needles with green fluorescence, m. p. 164°; the β-*naphthyl* isomeride, m. p. 195°, has a similar appearance. 5-*Phenyl*-1-p-*bromophenyl-3-styrylpyrazoline*, prepared in glacial acetic acid solution at the ordinary temperature, forms yellow needles with green fluorescence, m. p. 177°. *Distyryl ketone* p-*nitrophenylhydrazone*, yellowish-red leaflets, m. p. 173°, yields *p*-phenylenediamine by reduction with sodium amalgam, and is converted into 5-*phenyl*-1-p-*nitrophenyl-3-styrylpyrazoline*, yellowish-red crystals with intense green fluorescence, m. p. 204—205°, by boiling glacial acetic acid. *Di*-o-*methoxystyryl ketone phenylhydrazone*, brownish-yellow crystals, m. p. 142°, is converted into 1-*phenyl*-5-o-*methoxyphenyl*-3-o-*methoxystyrylpyrazoline*, pale yellow crystals with greenish-blue fluorescence, m. p. 153—154·5°, in a similar manner. 1-*Phenyl*-5-p-*methoxyphenyl*-3-p-*methoxystyrylpyrazoline*, prepared in boiling benzene, or, more simply, hot glacial acetic acid solution, forms pale yellow leaflets, m. p. 159°, which are so intensely fluorescent that they appear almost green. 1-*Phenyl*-5-p-*dimethylaminophenyl*-3-p-*dimethylaminostyrylpyrazoline* forms yellow needles, m. p. 192°, which exhibit an extraordinarily intense green fluorescence.

Di-o-*chlorostyryl ketone*, yellow needles, m. p. 125°, prepared from *o*-chlorobenzaldehyde and acetone in 5% boiling alcoholic sodium methoxide solution, reacts with *p*-bromophenylhydrazine by prolonged keeping in glacial acetic acid in the cold to form the p-*bromophenylhydrazone*, $C_{23}H_{17}N_2Cl_2Br$, dark yellow crystals, m. p. 145°, but yields by treatment with phenylhydrazine in boiling alcohol containing a little acetic acid 1-*phenyl*-5-o-*chlorophenyl*-3-o-*chlorostyrylpyrazoline*, yellow needles, m. p. 145°, forming a green, fluorescent solution in alcohol. 1-*Phenyl*-5-p-*chlorophenyl*-3-p-*chlorostyrylpyrazoline*, m. p. 212°, forms yellow needles with intense green fluorescence; its solution in concentrated sulphuric acid is so slightly coloured by ferric chloride that some doubt would exist as to the substance being a pyrazoline were it not that aniline is not

produced by its reduction by sodium amalgam. *Di*-p-*chlorostyryl ketone* p-*bromophenylhydrazone*, yellow needles, m. p. 183°, which become brown in air, yields *p*-bromoaniline by reduction with sodium amalgam, and is converted into 5-p-*chlorophenyl*-1-p-*bromophenyl*-3-p-*chlorostyrylpyrazoline*, yellow needles with intense green fluorescence, m. p. 173—174°, by boiling glacial acetic acid.

Methyl 5-*carbomethoxy*-1-*phenylpyrazoline*-3-*acrylate*,

$$\begin{array}{l}\mathrm{CH(CO_2Me){\cdot}CH_2} \\ | \\ \mathrm{NPh}\text{———————}\mathrm{N}\end{array}\!\!>\mathrm{C{\cdot}CH{:}CH{\cdot}CO_2Me},$$

m. p. 153°, yellow leaflets with a striking green fluorescence, is prepared from phenylhydrazine and methyl γ-keto-$\Delta^{\alpha\delta}$-pentadiene-αε-dicarboxylate (Straus, A., 1904, i, 851) in boiling benzene. The *ethyl ester*, $C_{17}H_{20}O_4N_2$, yellow, fluorescent leaflets, m. p. 92·5°, yields the *acid*, $C_{13}H_{12}O_4N_2$, yellow needles, m. p. 204° (decomp.), by hydrolysis with aqueous-alcoholic sodium hydroxide on the water-bath. The preceding methyl ketopentadienedicarboxylate forms a *phenylmethylhydrazone*, $C_{16}H_{18}O_4N_2$, dark red crystals, m. p. 105°, and the ethyl ester forms a p-*bromophenylhydrazone*, $C_{17}H_{19}O_4N_2Br$, reddish-yellow needles, m. p. 134°.

When boiled with glacial acetic acid, the phenylhydrazones of phenyl cinnamylidenemethyl ketone and of dicinnamylidenemethyl ketone are converted respectively into substances, $C_{23}H_{20}N_2$, colourless crystals with faint blue fluorescence, m. p. 123—124°, and $C_{27}H_{24}N_2$, orange-yellow needles, m. p. 142°, which are not pyrazolines because they cannot be oxidised to the pyrazolinecarboxylic acids.

Straus and Ackermann's *p*-chlorophenyl *p*-chlorostyryl ketone phenylhydrazone (A., 1909, i, 489) is really 1-phenyl-3:5-di-*p*-chlorophenylpyrazoline, and Minnuni's distyryl ketone phenylhydrazone (A., 1900, i, 237) is 1:5-diphenyl-3-styrylpyrazoline.

All the pyrazolines examined exhibited the most intense fluorescence when exposed to Röntgen rays. An apparatus is described by which several substances can be simultaneously but separately exposed to the rays with or without passage through zinc foil, and the intensities of the fluorescence compared with that of barium platinocyanide. The fluorescence is still visible after the rays have passed through zinc foil 0·6 mm. in thickness. A new noteworthy fact is that the fluorescence is observed, not only with the crystalline substances, but also with their solutions, the intensity being greatly influenced by the nature of the solvent. In the case of a 1% solution of the ester of 5-carboxy-1-phenylpyrazoline-3-acrylic acid, the solutions in alcohol and glacial acetic acid were only feebly fluorescent, and the fluorescence was destroyed by interposing zinc foil 0·2 mm. thick, but the solutions in carbon disulphide, benzene, and chloroform were intensely fluorescent, and a thickness of 1 mm. of zinc foil was necessary to destroy it.

There is a noteworthy difference between the fluorescence of the 1:3:5-trisubstituted pyrazolines excited by Röntgen rays and that produced by diffuse daylight. The excitation of Röntgen rays occurs

within narrow limits, and is connected with the presence of an unsaturated group (phenyl or carbonyl) in positions 3 and 5; if these positions are occupied by hydrogen or by an aliphatic group the pyrazoline fluoresces in diffuse daylight, but is unaffected by Röntgen rays. The effects on the intensity of the fluorescence of substituents in phenyl groups in positions 1, 3, and 5 are discussed. The phenylhydrazones of unsaturated ketones are intensely coloured, but do not exhibit a trace of fluorescence. C. S.

Preparation of Mercurous Amino-compounds. SCHWEIZ. SERUM- & IMPFINSTITUT (D.R.-P., 307893; from *Chem. Zentr.*, 1918, ii, 693).—The compounds are prepared by the action of one or more molecules of a mercurous salt on 1-phenyl-2:3-dimethyl-5-pyrazolone-4-sulphonamide. The *substance* obtained with mercurous sulphate (1 mol.) is a greyish-white, crystalline mass, which darkens and swells when heated; it is specifically lighter than mercurous sulphate, and contains 40% of mercury. On treatment with alkali it yields a precipitate of mercury and a soluble mercuric amino-compound, which is precipitated by hydrogen sulphide after acidification with hydrochloric acid. With two molecules of mercurous sulphate a complex *substance* is formed. The compounds are stable in substance and also when emulsified with fats. They have marked bactericidal and spirillocidal properties. H. W.

Salts of Helianthin. CHARLES R. STARK and WILLIAM M. DEHN (*J. Amer. Chem. Soc.*, 1918, **40**, 1573—1580).—Recent studies with methyl-orange (Dehn, A., 1917, i, 594) have led to the conclusion that colour changes in solution are largely or wholly independent of ionic concentrations. It has been suggested that the coloured solute forms additive compounds with acids, bases, or indifferent solvents. In the present communication it is shown that helianthin forms salts with great ease, all of which can be interpreted as additive compounds.

The helianthin salts of bases were prepared (1) from aqueous solutions of helianthin and the free base, (2) by double decomposition from methyl-orange and the salt of the base, (3) by adding helianthin to the pure liquid base, and (4) by treating helianthin with an excess of the base dissolved in absolute ether. In the preparation of helianthin salts with acids, the presence of water must be avoided; the salt is conveniently obtained by dissolving helianthin in excess of the warm acidic solvent and subsequently adding ether.

Salts of helianthin prepared in aqueous solution with inorganic bases always contain two molecules of water to each helianthin residue. The salts made with ammonia or volatile organic bases give free helianthin when heated; those containing the coloured ions Cr'', Cu'', Co'', Ni'', Fe'' or Fe''' give no evidence of the presence of these ions if they are judged only by the colour; when dehydrated, all helianthin salts containing the bivalent and tervalent metals, but not the univalent metals, tend to form the colour of helianthin itself. The salts of organic bases are always additive compounds of the type $C_{14}H_{14}N_3SO_3H$ base. The salts with the

ollowing metals or bases are described: *Aluminium*, golden, rhombic plates; ammonium, m. p. 225°, large golden-red, rhombic plates; *barium*, golden-brown, rhombic plates; *cadmium*, golden-red rhombic plates; *calcium*, orange needles and rhombic plates; *chromium*, golden-brown, rhombic plates; *cobalt*, golden-red, hexagonal and rhombic plates; *copper*, pale golden-brown, rhombic plates; *ferrous*, m. p. 209°, golden-brown, rhombic plates; *ferric*, reddish-golden, irregular and rhombic plates; *lead*, brown masses and irregular plates; *magnesium*, reddish-gold, hexagonal and rhombic plates; *manganese*, pale reddish-gold, irregular and rhombic plates; *silver*, dull brownish-red needles; *sodium*, m. p. 224°; *nickel*, light golden-red, hexagonal and rhombic plates; *potassium*, orange, hexagonal plates, m. p. 300°; *strontium*, brilliant orange, rhombic plates and needles; *uranium*, orange-red, rhombic plates; *zinc*, golden-brown, rhombic plates, m. p. 241°; *aniline*, golden-orange, prismatic flakes and needles, m. p. 211°; *benzidine*, golden-brown, irregular and rectangular plates and needles, m. p. 198° after changing at 194°; *brucine*, orange, prismatic needles, m. p. 224°; *cinchonidine*, light yellow, prismatic needles and irregular plates, m. p. 155°, after changing at 146°; *dimethylaniline*, needles and hexagonal plates; *methylaniline*, thin, golden-brown prisms and rhombic and hexagonal plates, m. p. 167°; *morphine*, bright orange, irregular plates and sheaves and wart-like masses of prisms, m. p. 219°; *α-naphthylamine*, dull brown needles, m. p. 211°; *β-naphthylamine*, brownish-yellow, thin, irregular plates, m. p. 209°; *phenylhydrazine*, orange needles and rectangular plates, m. p. 165°; *α-picoline*, dark brownish-red, rectangular and octagonal plates, m. p. 180°, after changing at 157°; *piperidine*, bright orange, octagonal and irregular plates, m. p. 223°; *quinine*, orange, amorphous mass, m. p. 158°; *quinoline*, orange-red prisms and octagonal plates, m. p. 194°; *strychnine*, golden-orange prisms and rectangular and irregular plates, m. p. 254°; o-*toluidine*, orange-red, prismatic needles, m. p. 203°; m-*toluidine*, golden-yellow needles and irregular plates, m. p. 202°.

Helianthin phenolate forms dark purple prisms, m. p. 200°.

The solubilities of the salts in water and their behaviour when heated are recorded in a series of tables, for which the original must be consulted. H. W.

Synthesis of some New Substantive Dyes derived from Benzidine-Sulphone. HUGH RYAN, JOSEPH ALGAR, and PHILIP O'CONNELL (*Proc. Roy. Irish Acad.*, 1918, **34**, (*B*), 85—96).—A series of dyes of the benzidine type has been prepared by coupling hydroxy- and amino-compounds with the tetrazo-derivative of benzidine-sulphone-disulphonic acid. The dyes have been isolated in the form of pure sodium salts; they act as direct dyes towards cotton and the colours are unaffected by washing. *Products* have been obtained with the following substances, the shade obtained on cotton being placed within brackets: naphthionic acid, dull blue, amorphous powder (purple); β-naphthylamine, red, amorphous

powder (violet-red); α-naphthylamine, dark red powder (navy blue); salicylic acid, reddish-brown powder (orange); "R" acid, reddish-blue powder (violet-red); "S" acid, red, amorphous powder (pink); "H" acid, dark blue powder (light blue); β-naphthol-6-monosulphonic acid, dark blue, amorphous powder (light purple); catechol, dark blue powder (light brown); resorcinol, dark blue powder (maroon); quinol, brown powder (buff); pyrogallol, chocolate-brown powder (buff); gallic acid, dark brown powder (light brown); sulphanilic acid, orange-red, amorphous powder (canary-yellow); dimethylaniline, dark blue powder (deep purple). H. W.

Influence of Substituents on Reactions. II. Rate of Reduction of Polymethylphenylhydrazines. HARTWIG FRANZEN, ARVID ONSAGER, and GUNNAR FAERDEN (*J. pr. Chem.*, 1918, [ii], **97**, 336—352. Compare A., 1918, i, 456).—Continuing the previous investigation, the authors have examined the rate of reduction by stannous chloride and hydrochloric acid of phenylhydrazines containing several nuclear methyl substituents. In the case of the dimethylphenylhydrazines the series, arranged in order of decreasing ease of fission, is precisely that which would be predicted from the previous results, the values of the constant K' being: 2:6-dimethylphenylhydrazine, 4·19; 2:4-, 2·49; 2:3-, 0·130; 2:5-, 0·107; 3:4-, 0·102. The 3:5-compound has been only provisionally examined, and its rate of reduction appears to be less than that of the 3:4-compound.

The only trimethylphenylhydrazines that have been examined are the 2:4:6- and 2:4:5-compounds. The entrance of yet another methyl group still further increases the ease of fission by stannous chloride and hydrochloric acid. These two compounds are reduced so rapidly at 100° that measurements cannot be made. At 80° the k' value of the former is 3·99 and of the latter 1·05. These values will be about six times as great at 100°, so that at this temperature 2:4:6-trimethylphenylhydrazine is reduced about six times more rapidly than 2:6-dimethylphenylhydrazine and about 1200 times more rapidly than phenylhydrazine itself.

The striking parallelism traced between the rate of reduction of substituted phenylhydrazines and the rate of dehalogenation of correspondingly substituted halogenobenzenes by hydriodic acid (*loc. cit.*) is still more evident in the case of the dimethylphenylhydrazines and the iododimethylbenzenes. After boiling with hydriodic acid for five hours the amounts of xylene obtained are: from 2-iodo-1:3-dimethylbenzene, 80%; from 4:1:3-, 60%; from 3:1:2-, trace; from 2:1:4-, trace; from 1:3:5-, 0%. 2-Iodo-1:3:5-trimethylbenzene yields 50% of mesitylene after boiling for five hours and 90% after being heated at 140° for five hours, the corresponding values for 5-iodo-1:2:4-trimethylbenzene being 0% and 85% of ψ-cumene respectively.

The polymethylphenylhydrazines required in the investigation were prepared by reducing the diazonium chlorides with stannous chloride and hydrochloric acid. In several cases the yields were

very bad, as low as 7·5%, in consequence of the reaction $ArN_2Cl + 2H = ArH + N_2 + HCl$ becoming the main reaction. A relation was found to exist between the rate of reduction of the polymethylphenylhydrazines and the tendency of the corresponding diazonium chlorides to yield the phenylhydrazine or the hydrocarbon and nitrogen on reduction; the more easily the phenylhydrazine is reduced the greater is the tendency of the corresponding diazonium chloride to yield the hydrocarbon and nitrogen on reduction.

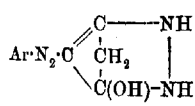
3-o-*Xylylhydrazine*, colourless needles, m. p. 108°, forms a *hydrochloride*, colourless leaflets, m. p. 208°, *benzylidene* derivative, $C_6H_3Me_2·NH·N:CHPh$, yellow crystals, m. p. 68°, p-*anisylidene* derivative, dark yellow, crystalline powder, m. p. 98°, and *dibenzoyl* derivative, $C_6H_3Me_2·NBz·NHBz$, colourless, crystalline powder, m. p. 198°. *Pyruvic acid* 3-o-*xylylhydrazone*,

$$CO_2H·CMe:N·NH·C_6H_3Me_2,$$

forms yellow leaflets, m. p. 166°.

2 : 4 : 6-*Trimethylphenylhydrazine hydrochloride* forms faintly yellow leaflets. C. S.

Synthesis of New Chloroarylhydrazones of Oxalomono-ester and -mono-amide Acid Chlorides and of the Corresponding Nitriles. CARL BÜLOW and RICHARD ENGLER (*Ber.*, 1918, **51**, 1246—1270).—In consequence of its decomposition by heat into carbon monoxide and ethyl malonate, ethyl oxalacetate is represented by the "aliphatic cyclic" structure, $CO<\begin{matrix}CH-CO_2Et\\ |\\ C(OH)·OEt\end{matrix}$ (compare Bülow and Huss, A., 1918, i, 314); citric acid, ethyl acetonedicarboxylate, ethyl formylacetate, ethyl acetoacetate, and acetylacetone are represented by similar 3-ring and 4-ring structures containing the group ·CH:C(OH)· similar to that in β-naphthol, and therefore reacting with diazonium salts. Ethyl o-tolueneazoacetoacetate, for example, is represented by the formula $\begin{matrix}C(OH):C·N_2·C_7H_7\\ |\quad\quad |\\ CH_2—C(OH)·OEt\end{matrix}$. This substance, previously prepared by Bülow and Schaub (A., 1908, i, 704), has m. p. 52° (Bülow and Schaub give 67°), yields the corresponding *potassium* salt, yellow needles, by hydrolysis with boiling 1% potassium hydroxide, and by treatment with concentrated nitric acid and subsequently with water is converted into nitrated o-toluenediazonium nitrate and ethyl acetoacetate. When treated with concentrated nitric acid in cold glacial acetic acid solution, however, it yields *ethyl nitro*-o-*tolueneazoacetoacetate*, needles, m. p. 135—136°, since the product and hydrazine hydrate in hot glacial acetic acid yield 4-?-*nitro*-o-*tolueneazo*-3-*methylpyrazolone*, yellowish-orange needles, m. p. 223—224° (decomp.). To azopyrazolones the authors give the formula (annexed).



By chlorination in cold alcoholic solution and repetition of the treatment on the initial product in warm alcohol, ethyl o-tolueneazoacetoacetate yields *ethyl* a-*chloroglyoxylate*

5-*chloro-o-tolylhydrazone*, $C_6H_3MeCl\cdot NH\cdot N:CCl\cdot CO_2Et$, colourless needles, m. p. 110°, which yields 5-chloro-*o*-toluidine by reduction with hydrochloric acid and zinc dust, and is converted by potassium cyanide in aqueous-alcoholic solution into *ethyl α-cyanoglyoxylate 5-chloro-o-tolylhydrazone*, $C_6H_3MeCl\cdot NH\cdot N:C(CN)\cdot CO_2Et$, golden-yellow needles, m. p. 163·5°, identical with the substance prepared by condensing diazotised 5-chloro-*o*-toluidine and ethyl cyano-acetate. The product obtained by the latter method is a labile form, which changes at its m. p., 106·5°, into the stable form, m. p. 163·5°. Ethyl α-chloroglyoxylate 5-chloro-*o*-tolylhydrazone resembles ethyl *o*-tolueneazoacetoacetate in its behaviour with concentrated nitric acid and exhibits halochromy when dissolved in concentrated sulphuric acid, the solution developing an intense yellow colour, which changes very rapidly to a dirty brownish-green, and regenerating the original substance on the addition of water. Ethyl α-cyanoglyoxylate 5-chloro-*o*-tolylhydrazone, by treatment with concentrated nitric acid at about 40—50° and subsequently with water, yields a nitrated product, m. p. 121—122°, together with a comparatively large amount of a diazonium nitrate.

By treatment with 96% alcohol and aqueous ammonia, ethyl *o*-tolueneazoacetoacetate yields, in addition to a small amount of the *ammonium* salt, m. p. 202° (decomp.), o-*tolueneazoacetoacetamide*, golden-yellow needles, m. p. 142°, which yields *nitro-o-tolueneazoacetoacetamide*, m. p. 243—244°, and only a trace of a diazonium salt by treatment with concentrated nitric acid at about 45°. The preceding ammonium salt yields *o-tolueneazoacetoacetic acid*, greenish-yellow needles, m. p. 137—138°, by treatment with glacial acetic acid.

Ethyl *p*-tolueneazoacetoacetate is very readily converted into the corresponding *potassium* salt by boiling 1—2% potassium hydroxide and resembles the ortho-isomeride in its behaviour towards concentrated nitric acid, yielding partly a diazonium salt by fission and partly *ethyl nitro*-p-*tolueneazoacetoacetate*, m. p. 143—144°, which is converted into 4-*nitro*-p-*tolueneazo*-3-*methylpyrazolone*, m. p. 234°, by hydrazine hydrate in glacial acetic acid solution.

Ethyl α-chloroglyoxylate 3-chloro-p-*tolylhydrazone*, m. p. 100°, is prepared like the preceding *o*-tolyl isomeride, but when chlorinated in carbon tetrachloride at 0° ethyl *p*-tolueneazoacetoacetate yields *ethyl α-chloroglyoxylate* p-*tolylhydrazone*, colourless needles, m. p. 101—101·5°. Both these hydrazones yield diazonium salts by treatment with nitric acid. The former reacts with potassium cyanide to form *ethyl α-cyanoglyoxylate 3-chloro*-p-*tolylhydrazone*, golden-yellow needles, m. p. 160°, which undergoes both nitration and fission by treatment with nitric acid, and in cold, alcoholic suspension reacts with chlorine in a unique manner, yielding 3-chloro-*p*-toluenediazonium chloride, ammonium chloride, and the decomposition products of ethyl hydrogen dichloromalonate. Ethyl α-chloroglyoxylate 3-chloro-*p*-tolylhydrazone yields 3-chloro-*p*-toluidine by reduction with hydrochloric acid and zinc dust. Ethyl α-cyanoglyoxylate 3-chloro-*p*-tolylhydrazone has also been prepared

by condensing diazotised 3-chloro-*p*-toluidine with ethyl cyanoacetate.

p-*Tolueneazoacetoacetamide*, prepared by treating an alcoholic solution of ethyl *p*-tolueneazoacetoacetate with a large excess of concentrated aqueous ammonia, forms pale green leaflets, m. p. 173°, yields *nitro*-p-*tolueneazoacetoacetamide*, m. p. 211—212°, and a little diazonium salt by treatment with concentrated nitric acid, and yields by chlorination in boiling alcoholic solution *α-chloroglyoxylamide* 3-*chloro*-p-*tolylhydrazone*, $C_6H_3MeCl\cdot NH\cdot N{:}CCl\cdot CO\cdot NH_2$, colourless needles; the constitution $C_6H_3MeCl\cdot NH<\begin{matrix} NH=CCl \\ | \quad\quad | \\ NH-CO \end{matrix}$ is suggested to account for the absence of colour. C. S.

Preparation of Bromolecithalbumin and Bromolecithin. PETER BERGELL (D.R.-P., 307490; from *Chem. Zentr.*, 1918, ii, 494—495).—Lecithalbumin is treated with bromine in anhydrous, indifferent organic solvents, and, when required, the bromolecithalbumin is decomposed into bromolecithin and albumin according to the method of converting lecithalbumin into lecithin. *Bromolecithalbumin* is a pale yellow, almost odourless powder with a faintly acid taste and reaction; it contains about 16·6% of bromine. It is transformed by methyl or ethyl alcohol, slowly in the cold more rapidly on warming, into albumin and *bromolecithin* containing up to 25% of bromine. H. W.

The Relationship between Diastase, Peroxydase, and Catalase. H. MAGGI (*Helv. Chim. Acta*, 1918, **1**, 433—451).—The simultaneous presence of peroxydase and catalase activity in many ferments has been attributed by Woker (A., 1917, i, 447) to the presence of an aldehydic group which unites with hydrogen peroxide to yield a secondary peroxide, $OH\cdot CHR\cdot O\cdot OH$, which has more powerful oxidising properties than hydrogen peroxide itself and also reacts with an excess of the latter to yield oxygen. The author has examined the question of the possibility of the aldehyde group being able to exert diastatic action, in addition to peroxydising and catalytic action, and suggests that the mechanism would consist in the alternate addition (to form a hydrate) and elimination of water.

The action of mixtures of starch and formaldehyde has been investigated by the capillarity method; the presence of dextrins is detected by means of iodine and of sugars by Fehling's solution. The results show that the behaviour of formaldehyde towards starch closely resembles that of diastase. One considerable difference, the recurrence of the blue coloration with lapse of time in the case of mixtures of formaldehyde and starch, has been further investigated. The phenomenon appears to be due to the formation of unstable iodine derivatives of formaldehyde or of the achroodextrins which gradually eliminate iodine. The following conditions are necessary: (i) unchanged starch, and (ii) a substance capable of liberating iodine, must be present; if these conditions are fulfilled, any

elimination of achroodextrins by combination, fission, or by any other method can restore the blue colour to the solution. H. W.

Nitro- and Amino-arylarsinic Acids. WALTER A. JACOBS, MICHAEL HEIDELBERGER and IDA P. ROLF (*J. Amer. Chem. Soc.*, 1918, **40**, 1580—1590).—The preparation of a number of nitro- and amino-arylarsinic acids is described; the nitro-compounds are generally obtained by Bart's method (D.R.-P., 250264), in which a diazo- or *iso*diazo-group is replaced by the arsinic acid residue. This procedure is particularly serviceable with *o*- and *p*-nitroamines; with *m*-nitroamines, on the other hand, the yields are poor, though better with *m*-nitrotoluidines than with *m*-nitroaniline. Reduction of the nitro- to the amino-group without disturbance of the arsinic acid residue is conveniently effected with cold, alkaline ferrous hydroxide solution (compare Benda, A., 1912, i, 63). The following compounds have been prepared by these methods:—*o*-nitrophenylarsinic acid, $NO_2 \cdot C_6H_4 \cdot AsO(OH)_2$, m. p. 235—240° (decomp.) [compare Bart, *loc. cit.*]; *o*-aminophenylarsinic acid (compare Benda, *loc. cit.*), needles, m. p. 153°; *m*-aminophenylarsinic acid (compare Bertheim, A., 1908, i, 590; Bertheim and Benda, A., 1912, i, 62), colourless, rhombic prisms, m. p. 213—215° (decomp.); *p*-nitrophenylarsinic acid (compare Bart, *loc. cit.*), pale yellow aggregates of minute leaflets, which do not melt below 275°; *p*-aminophenylarsinic acid; 2-*nitro*-p-*tolylarsinic acid*, faintly yellow, minute rods, m. p. 255—260° (decomp.); 2-*amino*-p-*tolylarsinic acid*, colourless needles, m. p. 180°, after softening and darkening; 6-*nitro*-o-*tolylarsinic acid*, pale yellow needles decomposing at 228—230°; 6-*amino*-o-*tolylarsinic acid*, rosettes or plates decomposing at 175—180°; 5-nitro-*p*-tolylarsinic acid (compare Michaelis, A., 1902, i, 411), cream-coloured needles which do not melt below 285°; 5-*amino*-p-*tolylarsinic acid*, microscopic needles, m. p. 172—175°; 5-nitro-*o*-tolylarsinic acid (compare Karrer, A., 1915, i, 333), m. p. 261—263° (decomp.), after melting or changing in appearance at about 225° according to the rate of heating; 5-*amino*-o-*tolylarsinic acid*, cream-coloured prisms decomposing at 235—245°; 4-*nitro*-o-*tolylarsinic acid*, minute needles, m. p. 235—240° (decomp.); 4-amino-*o*-tolylarsinic acid, microscopic needles, decomposing at 222—224° (Benda and Kahn, A., 1908, i, 591, give 180°); 4-*nitro*-p-*xylylarsinic acid*, yellow crystals, m. p. 290° (decomp.), which is not identical with the substance obtained by Michaelis (*loc. cit.*) by the nitration of *p*-xylylarsinic acid; 4-amino-*p*-xylylarsinic acid (compare Benda and Kahn, *loc. cit.*), colourless platelets, m. p. 213—214° (decomp.); 3-amino-4-hydroxyphenylarsinic acid, decomposing at 290° after darkening and softening at about 220°. H. W.

Silicon-Hydrocarbons with Nuclei containing Halogens, and their Use in Syntheses. GERHARD GRÜTTNER and MARIANNE CAUER (*Ber.*, 1918, **51**, 1283—1292. Compare Grüttner and Krause, A., 1918, i, 132).—An extension of the earlier work. Trichloro-*p*-bromophenylmonosilane reacts with alcohols to form

esters of the type $C_6H_4Br{\cdot}Si(OR)_3$, which react with magnesium to form organo-metallic derivatives of little value for synthetic purposes. The *methyl* ester, $C_6H_4Br{\cdot}Si(OMe)_3$, has b. p. 136°/13·5 mm., $D_4^{16\cdot5}$ 1·3525, D_4^{20} 1·3493, n_α 1·50791 n_D 1·51210 and n_β 1·52296 at 16·5°; *ethyl* ester, b. p. 149—150°/12 mm., $D_4^{16\cdot6}$ 1·2276, D_4^{20} 1·2244, n_α 1·48872, n_D 1·49247, n_β 1·50206 at 15·4°; *propyl* ester, b. p. 175—176°/14 mm., $D_4^{18\cdot8}$ 1·1564, D_4^{20} 1·1553, n_α 1·48144, n_D 1·48497, n_β 1·49386, n_γ 1·50129 at 16·6°; iso*butyl* ester, b. p. 190—191°/14 mm., $D_4^{17\cdot2}$ 1·0949, D_4^{20} 1·0923, n_α 1·47531, n_D 1·47865, n_β 1·48698, and n_γ 1·49424 at 14·9° (all densities are reduced to vacuum standard).

The magnesium compound of *p*-bromophenyltriethylmonosilane (*loc. cit.*) reacts badly with formaldehyde, smoothly with acetaldehyde (not paraldehyde), and tolerably well with higher aldehydes to form alcohols of the type $SiEt_3{\cdot}C_6H_4{\cdot}CHR{\cdot}OH$; the *ethanol* has b. p. 173—174°/14·5 mm., $D_4^{19\cdot5}$ 0·9601, D_4^{20} 0·9596, n_α 1·51404, n_D 1·51822, n_β 1·52885, n_γ 1·53810 at 17·2°; the *propanol* has b. p. 185°/16·5 mm., $D_4^{17\cdot0}$ 0·9603, D_4^{20} 0·9575, n_α 1·51243, n_D 1·51661, n_β 1·52734 at 18·0°; the n-*butanol* has b. p. 199—201°/21 mm., D_4^{14} 0·9546, D_4^{20} 0·9491, n_α 1·50373, n_D 1·50754, n_β 1·51737; the iso*butanol* has b. p. 190—192°/18 mm., $D_4^{17\cdot5}$ 0·9535, D_4^{20} 0·9512, n_α 1·50820, n_D 1·51212, n_β 1·52231 at 19·2°. By heating with fuming hydrochloric acid in a sealed tube at 90°, the ethanol gives a good yield of triethylsilicol, b. p. 70·5°/16·5 mm., $D_4^{19\cdot7}$ 0·8650, D_4^{20} 0·8647, n_α 1·43393, n_D 1·43639, n_β 1·44228, n_γ 1·44675 at 16·5°.

The magnesium compound of *p*-bromophenyltriethylmonosilane reacts with silicon tetrachloride in ethereal solution to form *trichloro*-p-*triethylsilylphenylmonosilane*, $SiEt_3{\cdot}C_6H_4{\cdot}SiCl_3$, b. p. 173—176°/13·5 mm., a colourless, highly refractive oil which has an offensive odour, fumes in air, and is at once hydrolysed by water. It reacts with magnesium ethyl bromide in ether to form *bis*-p-*triethylsilylbenzene*, $C_6H_4(SiEt_3)_2$, b. p. 195—196°/16·5 mm., $D_4^{17\cdot4}$ 0·8989, D_4^{20} 0·8967, n'_α 1·50555, n_D 1·50942, n_β 1·51945, n_γ 1·52788 at 15·7°, a colourless, mobile, not unpleasantly odorous liquid, which is converted by bromination in the presence of an iron catalyst into *p*-dibromobenzene and bromotriethylmonosilane.

The interaction of magnesium *p*-bromophenyl bromide and phenyltrichloromonosilane in ether leads to the formation of *phenyl*-p-*bromophenyldichloromonosilane*, $C_6H_4Br{\cdot}SiPhCl_2$, b. p. 199—200°/14 mm., $D_4^{18\cdot5}$ 1·5019, D_4^{20} 1·5005, n_α 1·60294, n_D 1·60921, n_β 1·62531, n_γ 1·63953 at 19°, which is converted by ethyl alcohol into the *diethoxy*-compound, $C_6H_4Br{\cdot}SiPh(OEt)_2$, b. p. 201°/17 mm., $D_4^{21\cdot5}$ 1·2474, D_4^{20} 1·2488, n_α 1·54525, n_D 1·55031, n_β 1·56322, n_γ 1·57467 at 19°, and *bisethoxyphenyl*-p-*bromophenyldisiloxane*, $(C_6H_4Br{\cdot}SiPh{\cdot}OEt)_2O$, b. p. 317—318°/20 mm., D_4^{22} 1·3350, D_4^{20} 1·3369, n_α 1·57867, n_D 1·58437, n_β 1·59895, n_γ 1·61146 at 18·6°. *Phenyl*-p-*bromophenyldiethylmonosilane*, $C_6H_4Br{\cdot}SiPhEt_2$, b. p. 203—203·5°/13·5 mm., $D_4^{19\cdot7}$ 1·2156, D_4^{20} 1·2153, n_α 1·57794, n_D 1·58351, n_β 1·59781, n_γ 1·61035 at 17·9°, and *phenyl*-p-*ethylphenyldiethylmonosilane*, $C_6H_4Et{\cdot}SiPhEt_2$, b. p. 169—170°/14 mm., $D_4^{19\cdot0}$ 0·98403, D_4^{20} 0·98310, n_α 1·55716, n_D 1·56225.

n_β 1·57559, n_γ 1·58713 at 16·8°, are obtained by the interaction of magnesium ethyl bromide and phenyl-*p*-bromophenyldichloromonosilane in ethereal solution, the product after distillation of the ether being heated at about 140° for three hours and then decomposed in the usual manner. Similarly, the product from magnesium ethyl bromide and trichloro-*p*-bromophenylmonosilane, after being heated at 180° for ten hours and then decomposed, yields p-*ethylphenyltriethylmonosilane*, b. p. 117—118°/18 mm., $D_4^{18·2}$ 0·8969, D_4^{20} 0·8950, n_α 1·50272, n_D 1·50671, n_β 1·51697, n_γ 1·52583 at 20·7°. C. S.

Organic Lead Compounds. VIII. Mixed Lead Aryl Alkyls of the Type $PbArR_3$. GERHARD GRÜTTNER and GERTRUD GRÜTTNER (*Ber.*, 1918, **51**, 1293—1298).—Such substances are obtained in accordance with the equation $PbR_3X + MgArX = PbArR_3 + MgX_2$, where X is a halogen atom; the diaryl hydrocarbons which are formed as by-products can be removed by freezing or by fractional distillation. Lead aryl trialkyls are colourless, refractive, faintly odorous oils which in the presence of air and in diffuse daylight do not decompose in the course of many months. They decompose above 200° with the separation of lead, and by treatment with bromine in ether at −75° lose the aromatic group, and sometimes also an alkyl group to a slight extent, lead trialkyl bromides and lead dialkyl dibromides being formed. The latter is the main product in the case of lead benzyl triethyl.

The following are described. *Lead phenyl trimethyl*, b. p. 104°/13 mm., $D_4^{23·7}$ 1·7342, D_4^{20} 1·7376, n_α 1·5753, n_D 1·5816, n_β 1·5988, n_γ 1·6138 at 23·7°; *lead* p-*tolyl trimethyl*, b. p. 118—119°/13 mm., D_4^{20} 1·6826, $D_4^{21·5}$ 1·6812, n_α 1·5672, n_D 1·5732, n_β 1·5895, n_γ 1·6039 at 20·0°; *lead* o-*tolyl trimethyl*, b. p. 117·5—118°/13 mm., $D_4^{21·4}$ 1·7395, D_4^{20} 1·7408, n_α 1·5734, n_D 1·5793, n_β 1·5954, n_γ 1·6095 at 21·4°; *lead phenyl triethyl*, b. p. 135°/12 mm., $D_4^{21·1}$ 1·5920, D_4^{20} 1·5931, n_α 1·5698, n_D 1·5757, n_β 1·5917, n_γ 1·6057 at 21·1; *lead* p-*tolyl triethyl*, b. p. 154·0°/13 mm., $D_4^{24·8}$ 1·5237, $D_4^{22·0}$ 1·5262, D_4^{20} 1·5281, n_α 1·5629, n_D 1·5686, n_β 1·5842, n_γ 1·5979 at 22·0°; *lead* o-*tolyl triethyl*, b. p. 153·5°/13 mm., $D_4^{21·5}$ 1·5839, D_4^{20} 1·5853, n_α 1·5682, n_D 1·5740, n_β 1·5897, n_γ 1·6035 at 21·5°; *lead benzyl triethyl*, b. p. 149—150·5°/13 mm., D_4^{23} 1·5374, $n_D^{21·4}$ 1·5843, appears to decompose slightly during distillaion, some dibenzyl being formed.

Lead α-*naphthyl triethyl* loses naphthalene at its b. p. 176°/13 mm. *Lead benzyl trimethyl* decomposes at 124°. C. S.

Organic Lead Compounds. IX. Lead Triphenyl Haloids. GERHARD GRÜTTNER (*Ber.*, 1918, **51**, 1298—1303).—An ethereal suspension of lead tetraphenyl in ether reacts with bromine at about −75° to form essentially a mixture of unchanged material and lead diphenyl dibromide, only about 10% of lead triphenyl bromide being formed. This result is doubtless to be attributed to the easy solubility of the monobromide and the sparing solubility of lead tetraphenyl, in consequence of which the first, when formed, is more readily attacked than the latter. When pyridine

at $-50°$ is used instead of ether (compare Krause, A., 1918, i, 415), an almost quantitative yield of *lead triphenyl bromide*, $PbPh_3Br$, colourless needles, m. p. 166°, is obtained. It is converted into the *iodide*, $PbPh_3I$, pale yellow prisms, m. p. 142°, by aqueous potassium iodide, and into the *oxide* by cold 10% aqueous alkali hydroxide. The oxide is converted quantitatively into the *chloride*, $PbPh_3Cl$, colourless needles or prisms, m. p. 206°, by 15% hydrochloric acid at the ordinary temperature, and from a concentrated alcoholic solution of the latter, hydrogen sulphide precipitates the *sulphide*, $(PbPh_3)_2S$, as a white precipitate. C. S.

Physiological Chemistry.

The Consumption of Oxygen and Production of Carbon Dioxide in the Blood of Dogs. I. L. BERCZELLER (*Biochem. Zeitsch.*, 1918, **90**, 294—301).—Sterile blood was kept under mercury or paraffin at 38°, and when fresh, and after keeping for various intervals, the oxygen and carbon dioxide were estimated by Barcroft's method. The production of carbon dioxide was generally found to be greater than the oxygen consumption. Similar experiments were carried out in the presence of dextrose. Here, again, there was no direct relationship between oxygen consumption and carbon dioxide production. There was a much larger oxygen consumption and carbon dioxide production than in normal blood.

S. B. S.

Analysis of Blood Gases. II. Hæmoglobin as an Indicator. The Theory of Indicators. H. STRAUB and KLOTHILDE MEIER (*Biochem. Zeitsch.*, 1918, **90**, 305—336).—There is a discontinuity of the curve expressing the amount of carbon dioxide taken up by the blood (hæmolysed by saponin freezing, etc.) plotted against the carbon dioxide tension. This discontinuity does not follow the ordinary laws of mass action, but begins when $p_H = 7{\cdot}0$, at which point one molecule of carbon dioxide is taken up by one molecule of hæmoglobin. This indicates that when $p_H > 7{\cdot}0$ the hæmoglobin molecules carry a negative charge, which they lose as soon as $p_H = 7$. When $p_H = 6{\cdot}39$, a second point of discontinuity is reached in the curve, which indicates that at this point the hæmoglobin molecules acquire a positive charge. These phenomena are explained in reference to the charges carried by the colloidal particles, and not by the laws of mass action, for the position of the bends in the curve depends also on the presence of other ions than those of hydrogen. Univalent anions and cations, and bivalent cations exert no influence on the position of the bend; tervalent anions shift the position of the first bend from $p_H = 7{\cdot}00$ to $p_H = 6{\cdot}80$,

and are without action on the position of the second bend. Tervalent cations also exert a strong influence on the position. The application of these facts to the use of hæmoglobin as an indicator is discussed. S. B. S.

The Influence of Narcotics on the Permeability of Blood-corpuscles for Dextrose and Carbamide. GERTRUD KATZ (*Biochem. Zeitsch.*, 1918, **90**, 153—165).—The entrance of dextrose into human blood corpuscles is not inhibited by the narcotics heptyl alcohol and thymol. The entrance of carbamide into ox-corpuscles is delayed by thymol. S. B. S.

The Part Played by Acid in Carbohydrate Metabolism. III. Acid and the Glycogen of the Muscles. H. ELIAS and E. SCHUBERT (*Biochem. Zeitsch.*, 1918, **90**, 229—243).—The glycogen content of the muscles of dogs' legs differs, the right from the left, by about 2—3% in the mean. Interarterial injection of lactic acid over several hours does not reduce to any appreciable extent the amount of glycogen; the muscle glycogen appears to be far more resistant to external stimuli than does the liver glycogen.
S. B. S.

Salivary Amylase. I. A Preliminary Experimental Study of its Stability in Saliva. ROLLIN C. MYERS and LEONARD C. SCOTT (*J. Amer. Chem. Soc.*, 1918, **40**, 1713—1716).—Salivary amylase in sterilised saliva without preservative is found to be relatively stable for a year. The relative stability may vary from practically no change to that of more than 50% of its former amyloclastic activity, the variation depending probably on slight differences in the composition of the saliva.

The causes which lower the stability of salivary amylase in saliva are not solely the degrading action of bacteria, mould spores, yeast plants, and special preservatives. The inherent chemical weakness of the enzyme molecule must be taken into account, which weakness may be increased by the maintenance of temperatures from 18° to 30°, by diffused light and by compounds in the saliva.

Salivary amylase in saliva is relatively stable for a year when preserved with toluene, thymol, and chloroform. Toluene has the least destructive action on the enzyme, and thymol and chloroform follow in order.

Saliva may be kept for two and a-half years under the ordinary laboratory conditions without preservative, and may still show a form of amyloclastic activity. H. W.

The Presence of Food Accessories in Urine, Bile, and Saliva. A. M. MUCKENFUSS (*J. Amer. Chem. Soc.*, 1918, **40**, 1606—1611).—As a result of a series of experiments on pigeons with acute symptoms of polyneuritis, the author is led to the conclusion that the antineuritic vitamine is probably present in comparatively small quantity in clean, fresh, filtered bile from the

bladder of the ox, and that traces of it appear to be present in fresh filtered human urine. H. W.

Fischer's Theory of Water Absorption in Œdema. W. J. CROZIER (*J. Amer. Chem. Soc.*, 1918, **40**, 1611—1612. Compare Fischer, A., 1918, i, 129, 130, 131; Henderson and Cohn, *ibid.*, i, 316).—The author has carried out a series of experiments on the intracellular acidities in the tissues of three species of sponges, one echinoderm, and a nudibranch mollusc. The observations made increase the difficulties in the way of accepting Fischer's conception of water metabolism, since they indicate a range of intracellular acidities, in animal tissues, within which it is known that no significant protein swelling occurs, and since they show that an intracellular acidity even remotely approaching that at which significant swelling might be possible is irreversibly associated with natural death. H. W.

The Storage and Excretion of Arsenic after Administration by Salvarsan in Serum and Water. HANS BERGMANN (*Biochem. Zeitsch.*, 1918, **90**, 348—360).—The author investigated the rate of excretion of arsenic excreted in the urine of man after administration of neosalvarsan in serum (human) and in aqueous solutions. In the latter case the excretion is much greater. Experiments are quoted which tend to show that the salvarsan undergoes chemical change more rapidly in aqueous solution than in serum. A series of experiments is also described, in which the accumulation of arsenic in the organs of rabbits after administration of salvarsan was investigated. They tend to indicate a greater accumulation after administration of the drug in serum. S. B. S.

Chemistry of Vegetable Physiology and Agriculture.

A Bacterium present in Water and in Bitter Wines which is capable of Dehydrating Glycerol. A New Reaction for Glycerol. E. VOISENET (*Ann. Inst. Pasteur*, 1918, **32**, 476—510. Compare A., 1914, i, 462).—The new bacterium, termed *Bacillus amaracrylus*, is related to *B. coli* and *B. typhosus*, but is not pathogenic. When cultivated in dextrose solution, it forms carbon dioxide and hydrogen, like *B. coli*, but it does not form indole from tryptophan. Inoculation of a medium containing glycerol with the new bacterium results in the production of acraldehyde, which is its characteristic reaction. H. W. B.

The Inter-relationship of certain processes in Metabolism of Bacillus coli communis. FRITZ VERŽER (*Biochem. Zeitsch.*, 1918, **91**, 1—45).—Three main series of investigations were

instituted: (1) The influence of certain poisons on the different processes, (2) the influence of one metabolism product on the formation of others, (3) the regulation of the formation of a product by its own accumulation. The processes investigated were (*a*) gas formation from dextrose, (*b*) acid formation from dextrose and lactose, (*c*) indole formation, (*d*) reducing action on dyes, (*e*) multiplication of the bacteria.

(1) Protoplasmal poisons, phenol, formaldehyde, and mercuric chloride inhibit all the processes in about the same concentration. Crystal-violet shows slight inhibition of gas formation, but strong inhibition of reducing processes. The respiratory poison, potassium cyanide, inhibits strongly gas formation and still more strongly reduction processes and indole formation in concentrations in which the acid formation is not affected. The narcotic, chloroform, inhibits respiration, but not as strongly as potassium cyanide; in contrast to the latter, it also inhibits acid formation. Alcohol acts, but less strongly, like chloroform. The author draws the conclusion that the only really essential vital process is the formation of acid from dextrose.

(2) From the study of the presence of acid on indole formation it was found that the latter is inhibited entirely by the presence of acids, and is only normally produced from proteins or peptones by the bacteria in the absence of dextrose; scission of this by the bacteria produces acid to inhibit indole formation.

(3) The influence of the presence of acids and alkalis on the further formation of acids by the bacteria was investigated. It was found that when the acid in the culture medium reached a certain concentration, further formation of acid was inhibited, and also further formation of carbon dioxide, and multiplication of bacteria. If sugar insufficient to produce the amount of acid necessary for inhibitions is present, alkali formation sets in, until the medium attains a slightly alkaline reaction, when further formation of alkali is inhibited. The formation takes place only in presence of oxygen. From acid (except formic acid) no gas is formed either after reaching its maximum concentration or during formation of alkali. Inhibition of oxidation causes a compensatory increased production of acid. S. B. S.

Phytochemical Reductions. XIII. Asymmetrical Reduction. Conversion of Racemic Valeraldehyde (*dl*-α-Methylbutaldehyde) into *l*-Amyl Alcohol. C. Neuberg and M. Ringer (*Biochem. Zeitsch.*, 1918, **90**, 388—394).—The amyl alcohol produced from *dl*-α-methylbutaldehyde by a sugar–yeast fermentation mixture is lævorotatory. S. B. S.

The Method of Formation of Succinic Acid in Nature. III. Conversion of Aldehydopropionic Acid into Succinic Acid by Yeast. C. Neuberg and M. Ringer (*Biochem. Zeitsch.*, 1918, **91**, 131—136).—By means of maceration juice, and in absence of air, aldehydopropionic acid can be converted into succinic acid.

The conversion of glutamic acid into succinic acid follows, therefore, the following stages:

$$CO_2H\cdot CH_2\cdot CH_2\cdot CH(NH_2)\cdot CO_2H \longrightarrow CO_2H\cdot CH_2\cdot CH_2\cdot CO\cdot CO_2H \longrightarrow$$
$$CO_2H\cdot CH_2\cdot CH_2\cdot CHO \text{ (aldehydopropionic acid)} \longrightarrow CO_2H\cdot CH_2\cdot CH_2\cdot CO_2H.$$

All these stages except the first, which takes place, as far as investigations have gone, only in the living cell, can be accomplished by purely enzymatic reactions. S. B. S.

Physiological Investigation of a New Yeast which Flourishes in Tanning Liquors. TŌICHI ASAI (*J. Coll. Sci. Imp. Univ. Tokyo*, 1918, **39** (7), 1—42).—The new yeast, designated *Mycoderma tannica*, forms dark brown or brownish-black spots on leather undergoing the tanning process. The isolated yeast can be cultivated in a solution containing dextrose or lævulose or other carbohydrate, and an ammonium salt or amino-acid as a source of nitrogen. It does not readily grow in a dilute pure tannin solution, but when dextrose and aspartic acid are also present, rapid decomposition of the tannin occurs, owing to the excretion of tannase into the surrounding medium. The growth of the yeast is attended by the production of small quantities of alcohol and carbon dioxide, indicating the presence of zymase. Addition of tannin to the medium increases slightly the alcoholic fermentation. H. W. B.

Kinetics of the Cell-free [Fermentation [by Zymase]. OTTO MEYERHOF (*Zeitsch. physiol. Chem.*, 1918, **102**, 185—225). —The addition of sugar to an extract of dried yeast containing zymase, but free from cells, is succeeded by a period of quiescence, during which no sign of fermentation is observable. The interval which elapses between the addition of the sugar and the first appearance of fermentation is termed the "induction period." The duration of the induction period is determined by various factors; it is shorter for sucrose than for either dextrose or lævulose; it can be shortened by previously warming the sugar solution with disodium hydrogen phosphate or by grinding the dried yeast with glass powder. The presence of a small amount of hexose phosphate abolishes the induction period.

The rate of fermentation is dependent on the amount of free phosphate present. Increasing the amount of disodium hydrogen phosphate reduces the rate at which the velocity of fermentation increases, but the maximum velocity eventually attained is higher than in the absence of free phosphate until a certain maximum amount of the phosphate is reached; further addition of the phosphate then reduces the maximum velocity of fermentation attainable. The addition of other salts, such as sodium chloride, produces similar effects on the velocity of fermentation. The free phosphate functions, therefore, as a salt as well as exerting its specific zymase-activating action.

Hexose phosphate exerts an accelerating action on fermentation in proportion to its concentration, due to the decomposition of the ester itself. Fermentation is accelerated also by the addition of co-ferment in the form of boiled yeast juice; the extent to which it is affected depends on the concentration, and not on the absolute quantity of the co-ferment present in relation to zymase.

The inhibiting influence of narcotics on the fermentation of dextrose by zymase is somewhat intensified by the addition of salts. H. W. B.

Rôle of the Phosphate in Alcoholic Fermentation. HANS EULER and S. HEINTZE (*Zeitsch. physiol. Chem.*, 1918, **102**, 252—261).—The esterification of phosphoric acid by dried yeast in the presence of a protoplasmic poison, such as phenol, is related to the amount of water remaining in the yeast after the drying process. The maximum esterification is observed when dried yeasts containing from 10 to 15% of moisture are employed. Increasing the quantity of yeast used in the individual experiments appears to occasion a much greater increase in the amount of hexose phosphate produced. H. W. B.

Fumaric Acid Fermentation of Sugar. C. WEHMER (*Ber.*, 1918, **51**, 1663—1668).—*Aspergillus fumaricus* smoothly ferments relatively large quantities of sugar, yielding, in addition to a little citric acid, fumaric acid in the free state; the solution turns Congo-paper blue and dissolves calcium carbonate. Oxygen is necessary and, for continuous fermentation, calcium carbonate. Thus 20 grams of sugar (20% solution) and 2·87 grams (dry weight) of *Aspergillus fumaricus* dissolve 15 grams of calcium carbonate and produce about 33 grams of calcium salts consisting chiefly of the sparingly soluble normal calcium fumarate, but containing also varying quantities of the easily soluble hydrogen fumarate, about 4% of calcium citrate, and the calcium salt of another, unidentified acid. The sugar is fermented completely, and 60—70% of it is converted into acids. The optimum temperature is about 22°, the maximum about 30°. C. S.

Behaviour of Organic Compounds in Plants. X. G. CIAMICIAN and C. RAVENNA (*Gazzetta*, 1918, **48**, i, 253—304. Compare A., 1918, i, 473).—The first part of this paper, dealing with the action of certain compounds on the germination and development of plants, has been already abstracted.

The second part describes further investigations on the oxidation of organic compounds by the agency of enzymes contained in spinach leaves. The results of experiments in an atmosphere of carbon dioxide show that the disappearance of certain substances in an atmosphere of oxygen as a result of the action of such enzymes is due to an oxidation process.

In an atmosphere of carbon dioxide, saligenin is converted into the polyanhydride saliretin, this change being effected more

promptly by apple pulp than by spinach leaves. Ethyl alcohol and mannitol are not sensibly oxidised. Acetaldehyde, which undergoes little auto-oxidation in an atmosphere of oxygen, is not affected by the presence of the enzyme. The oxidation of acetone to formic and acetic acids under the influence of light is catalysed by the presence of the enzyme. Of the three amino-acids examined, glycine, alanine, and asparagine, only the last is oxidised by the enzyme in an atmosphere of oxygen, no change occurring in carbon dioxide. Cinnamic acid is not oxidised at the double linking, only minimal traces being transformed into the isomeric *iso*cinnamic acid; this isomerisation does not occur in carbon dioxide. Of the alkaloids examined, caffeine and strychnine remain unchanged, whereas morphine, quinine, and cinchonine are largely oxidised.

The enzymes of spinach leaves are also able to determine certain other reactions. Thus, in oxygen, dextrose is completely oxidised, probably to carbon dioxide, whilst in carbon dioxide it yields a substance giving dextrose on hydrolysis with acid. Further, in either oxygen or carbon dioxide, tartaric acid undergoes change, partly into a compound yielding tartaric acid under the action of emulsin.

The results of the experiments described in the third part of the paper show that, when inoculated into the living plant (maize), pyridine and nicotine are partly eliminated through the leaves, the transformation of further quantities by the plant being also indicated, but not definitely proved. T. H. P.

The Influence of Immersion in certain Electrolytic Solutions on Permeability of Plant Cells. MAUD WILLIAMS (*Ann. Bot.*, 1918, **32**, 591—599).—Cells of London Pride (*Saxifraga umbrosa*) petioles, after immersion in solutions of certain electrolytes, were found to be permeable to a 0·2% solution of ferric chloride, the entrance of the ferric chloride being indicated by formation of a blue colour with the tannin contained in these cells. The time of immersion in a given solution necessary to produce this abnormal permeability varied with the electrolyte and its concentration. In the cases of aluminium and potassium chlorides, and potassium and barium nitrates, the results obtained could be expressed approximately by the equation

$$\log T = K - A(\log C + 1),$$

where T is the time of immersion in the solution of the electrolyte needed to produce the abnormal permeability, C is the concentration in gram-mols. per litre, K is an independent constant, and A a constant depending on the electrolyte used. Abnormal permeability with respect to ferric chloride was not always accompanied by permeability to the rose-coloured pigment frequent in the sap of the cells. W. G.

The Occurrence of Melezitose in a Manna from the Douglas Fir. C. S. HUDSON and S. F. SHERWOOD (*J. Amer. Chem. Soc.*, 1918, **40**, 1456—1460).—A sample of manna from

the Douglas fir yielded about 50% of pure crystalline melezitose, and there is evidence that it contained sucrose and some reducing sugar, probably a mixture of dextrose with a smaller quantity of lævulose. The composition of the sample of dry manna was approximately: melezitose 75—83%, sucrose 2·9%, reducing sugars 11·5%. At present, the only other known natural source of melezitose in any quantity is the Tarkestan manna (Tarandjabine), which is, however, considerably inferior to the Douglas fir product in point of yield. H. W.

Occurrence of Allantoin in the Rhizome of Symphytum officinale and other Borraginaceæ. ALFRED VOGL (*Pharm. Post.*, 1918, **51**, 181—184; from *Chem. Zentr.*, 1918, ii, 36).—Large quantities of allantoin crystals, in the form of monoclinic prisms, are found in the rhizome of *Symphytum officinale.* The author has also succeeded in identifying allantoin crystals in the sections of the rhizome and has determined their distribution in the tissue. Crystallisation in the sections is best effected by pouring on them alcohol containing acetic acid (20%), covering with a cover-glass, and sealing with paraffin. The allantoin content of the rhizome of *S. officinale* varies with the time of year; it is at a maximum from autumn to early spring, at a minimum in the height of summer. The rhizomes of *S. tuberosum*, *S. cordatum*, *S. caucasicum*, and other *Borraginaceæ* appeared to be free from allantoin, possibly owing to unfavourable supply of material. H. W.

Action of Ammonium Salts on Plants. I. H. G. SÖDERBAUM (*Kungl. Landtbruks-Akad. Handlingar*, 1917, **56**, 537—561; from *Physiol. Abstr.*, 1918, **3**, 351).—This paper reports experiments with small grains and potatoes grown in pots, using ammonium salts as fertilisers; sodium nitrate was used in part for control purposes. The favourable influence of these salts on the total yield ranks as follows: diammonium hydrogen phosphate, ammonium carbonate, sulphate, nitrate, sodium nitrate, ammonium chloride. The phosphate gave a crop four times as large as an equivalent amount of the sulphate; the chloride proved very disadvantageous. Up to a certain limit, the addition of ammonium sulphate gave a progressively increased yield, but when the limit had been passed, there was a marked decrease. The adverse action of an excess of the salt was not the same in the case of each plant. Rye and potatoes were least sensitive in this respect, and wheat and barley most so, whilst oats occupied an intermediate position. Where there is neither soil acidity nor a deficiency of calcium, ammonium sulphate may be used to advantage in the field, as the amount applied in practice does not reach the limit where toxicity manifests itself. H. W. B.